AD NUMBER
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AUTHORITY
U.S. Army Environmental Center, APG, MD ltr, 15 Sep 2006

UNCLASSIFIED

AD NUMBER

ADB093506

NEW LIMITATION CHANGE

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Distribution authorized to U.S. Gov't. agencies and their contractors; Administrative/Operational Use; JUN 1985. Other requests shall be referred to Commander, Army Toxic and Hazardous Materials Agency, USATHAMA AMXTH-TE, Aberdeen Proving Ground, MD 21010.

FROM

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AUTHORITY

USATHAMA, per DTIC Form 55

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REPORT AMXTH-TE-TR-85012

DEVELOPMENT OF NOVEL DECONTAMINATION TECHNIQUES FOR CHEMICAL AGENTS (GB, VX, HD) CONTAMINATED FACILITIES

Phase II - Laboratory Evaluation of Novel Agent Decontamination Concepts

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JUNE 21, 1985

TASK FINAL REPORT FOR THE PERIOD AUGUST 1983 TO MARCH 1985

Distribution limited to U.S. Government Agencies only because of test and evaluation; June 1985. Other requests for this document must be referred to: Commander, USATHAMA AMXTH-TE APG, MD 21010

Prepared for:

U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
ABERDEEN PROVING GROUND, MARYLAND 21010

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3. DISTRIBUTION / AVAILABILITY OF REPORT
Distribution limited to U.S. Government agencies because of test and evaluation, June, 1985.

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

5. MONITORING ORGANIZATION REPORT NUMBER(S)
AMXTH-TE-TR-85012

6a. NAME OF PERFORMING ORGANIZATION
BATTELLE COLUMBUS LABORATORIES

6b. OFFICE SYMBOL (If applicable)

7a. NAME OF MONITORING ORGANIZATION
U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY

6c. ADDRESS (City, State, and ZIP Code)
505 KING AVENUE
COLUMBUS, OHIO 43201

7b. ADDRESS (City, State, and ZIP Code)
ABERDEEN PROVING GROUND, (EA) MD 21010-5401

8a. NAME OF FUNDING / SPONSORING ORGANIZATION

8b. OFFICE SYMBOL (If applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
DAAK11-81-C-0101

8c. ADDRESS (City, State, and ZIP Code)

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO	TASK NO.	WORK UNIT ACCESSION NO

11. TITLE (Include Security Classification)
Development of Novel Decontamination Techniques for Chemical Agents Contaminated Facilities Phase II Laboratory Evaluation of Novel Agent Decontamination Concepts

12. PERSONAL AUTHOR(S)
E.R. Zamejc, E.J. Mezey, T.L. Hayes, D.K. Wetzel, B.C. Garrett

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
FINAL REPORT	FROM 11/83 TO 3/85	1985, June 21	656

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
Chemical Agents, HD, Hot Gases, Oxime, GB, Decontamination, Steam, Flashblast, VX, Structures, OPAB, Ammonia

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Hot gases, steam, FREON®, vapor circulation, flashblast, monoethanolamine, ammonia, ammonia/steam, and an aqueous solution of n-octylpyridinium 4-aldoxime bromide (OPAB) were experimentally evaluated for their effectiveness in decontaminating HD, GB and VX. Emphasis was placed on the concepts ability to decontaminate these agents spiked onto painted and unpainted mild and stainless steels and unpainted porous materials. The experimental data demonstrated that the hot gas, steam and OPAB concepts were effective decontaminants for each agent/material combination investigated.

An engineering/economic analysis suggested that either hot gas or steam decontamination of field structures contaminated throughout with agent is feasible. Specific applications for OPAB were identified. In terms of cost, the hot gas concept is preferred over the steam concept.

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

22a. NAME OF RESPONSIBLE INDIVIDUAL
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22c. OFFICE SYMBOL
AMXTH-TE-D

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

Block 18: (Continued)

Monoethanolamine
FREON 113®
Concrete
Steel
Alkyd Paint
Diffusion
Spary
Analytical Method Development
Engineering and Cost Analyses
Agent Decomposition Products

Block 19: (Continued)

Analytical method development activities indicate that HD, GB and VX interact with concrete. The interaction, possibly a chemical reaction, may obviate the need to decontaminate unpainted concrete in the field, especially in the case of the nerve agents GB and VX.

ACKNOWLEDGEMENTS

The authors of this report are grateful for the efforts of Paula Gayness, Sandy Jennings, and Karen Lynn for the preparation of this document and for the efforts of John Young, Fleet Girod, Jerry Nichols, and Fred Moore for their assistance in performance of the experiments.

EXECUTIVE SUMMARY

As part of their responsibilities in DOD real property disposal, USATHAMA must identify, contain and eliminate toxic and hazardous materials where facilities, potentially available for alternate government or private use, have been declared excess or are candidates for excessing. With this mandate USATHAMA must provide not only the technical basis to implement decontamination but also the standards to insure decontamination has been effective. Battelle's Novel Processing Technology Program supported USATHAMA through identification, development, and recommendation of decontamination methods for Army facilities which have been contaminated with chemical warfare agents.

In a first phase study about 65 decontamination concepts were generated, described in detail, and rank/ordered. The most promising concepts were recommended for further evaluation - hot gases, FREON® vapor circulation, flashblast, monoethanolamine, steam, ammonia, ammonia/steam, and an aqueous solution of n-octylpyridinium 4-aldoxime bromide (OPAB).

In this second phase study, the selected concepts were experimentally evaluated for their effectiveness in decontaminating HD, GB and VX. Emphasis was placed on the concepts ability to decontaminate these agents spiked onto painted and unpainted mild and stainless steels and unpainted porous materials. The experimental data demonstrated that the hot gas, steam and OPAB concepts were effective decontaminants for each agent/material combination investigated. Each of the other techniques (i.e., flashblast, ammonia, etc.) was effective to some extent, but either the effectiveness was limited to specific agent/material combinations or the concept appeared less promising.

An engineering/economic analysis suggested that either hot gas or steam decontamination of field structures contaminated throughout with agent is feasible. In terms of cost, the hot gas concept is preferred over the steam concept. As such, the hot gas concept was recommended as the primary decontamination concept for field evaluations in Phase 3 of the program. The steam and OPAB concepts were also recommended for Phase 3 evaluations. That is, OPAB is recommended for use as a protective coating

and as a non-corrosive decontaminant for inside of pipes, sumps, and other equipment; steam should be retained as a back-up to the hot gas concept.

Analytical method development activities indicated that HD, GB and VX interact with concrete. The interaction, possibly a chemical reaction, (i.e., hydrolysis) may obviate the need to decontaminate unpainted concrete in the field, especially in the case of the nerve agents GB and VX. The need for agent impermeable paint on concrete in future agent demilitarization facilities should also be reconsidered because of this apparent reaction (i.e., paint may not be necessary).

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on

DEVELOPMENT OF NOVEL DECONTAMINATION TECHNIQUES FOR CHEMICAL AGENT (GB, VX, HD), CONTAMINATED FACILITIES - PHASE 2

to

UNITED STATES ARMY
TOXIC AND HAZARDOUS MATERIALS AGENCY

from

BATTELLE
Columbus Laboratories

June 21, 1985

1.0 INTRODUCTION

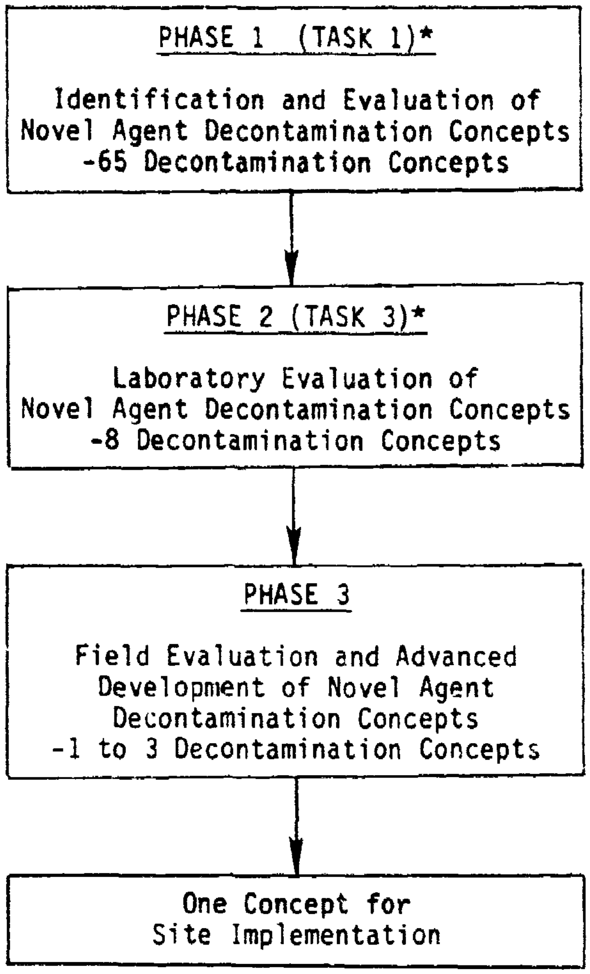
As part of their responsibilities in DOD real property disposal, the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) must identify, contain, and eliminate toxic and hazardous materials and related contamination where lands and facilities, potentially available for alternate government or private use, have been declared excess or are candidates for excessing. With this mandate USATHAMA is to provide the technical basis to implement the decontamination and also provide the standards to insure decontamination has been effective. Facilities which might require such decontamination are located at Tooele Army Depot, Rocky Mountain Arsenal, and Edgewood Area of Aberdeen Proving Ground. Of concern are contaminated building structures, underground and above ground storage tanks, reaction vessels, sumps, waste stream conduits, and pipes. Both the exposed surfaces of the materials as well as the interior areas into which chemical warfare agents have penetrated (i.e., through cracks, pores, or other openings) may require decontamination.

USATHAMA envisions that new, improved procedures for the decontamination of facilities previously utilized for chemical agent manufacture or testing will be required. The only currently approved method of decontaminating materials involves incineration at a temperature of 1000 F for a period of 15 minutes. Materials exposed to such conditions are described as having attained the 5X status and are defined as suitable for unrestricted use. Unfortunately, the time and expense required to accomplish such decontamination is immense. Successful development of an alternative decontamination technique which would not require the dismantling of a facility and which would result in a 5X decontamination status rating (or its equivalent) without incineration represents a potentially large cost savings to the Government.

USATHAMA tasked Battelle Columbus Laboratories in the Novel Processing Technology Program to identify and develop treatment methods and to recommend plans for carrying out the decontamination. The ideal concept would be a single method that is both universally applicable and most cost effective. Decontamination of structures and equipment contaminated with chemical agents to a level that does not pose a hazard during unrestricted use, represents an extremely difficult problem in any excessing action. This document details the efforts of Phase 2 of USATHAMAs three phase research and development program for the restoration of chemical warfare agent installations. A description of the program which leads to site implementation of one decontamination concept is given in Figure 1.

1.1 Phase 1 Results

In the first phase study, about 65 concepts (See Table 1) were generated and described in sufficient detail to permit their evaluation against the criteria of mass transfer, destruction efficiency, safety, damage to structures, penetration depth, applicability to complex structures, operating costs, capital costs, and waste treatment costs.(1) This evaluation was the basis for the selection of the most promising concepts for experimental evaluation in the second



* Task 2 and 4 were parallel efforts focusing on explosive decontamination concepts.

FIGURE 1. DESCRIPTION OF RESEARCH AND DEVELOPMENT PROGRAM FOR AGENT INSTALLATION RESTORATION

TABLE 1. AGENT DECONTAMINATION CONCEPTS EVALUATED DURING PHASE I

CHEMICAL

OCTYL PYRIDINIUM 4-ALDOXIME BROMIDE (OPAB)
DS2 (A)
CD-1 (B)
SUPERTROPICAL BLEACH (STB)
ALL PURPOSE DECONTAMINANT (APD) (C)
MONOETHANOLAMINE
GAMMA RADIATION
NITRIC ACID
AMMONIUM HYDROXIDE
HYPOCHLORITES
DANC
GASEOUS AMINES
CHLORINE
STEAM
AMMONIA/STEAM
PERCHLORYL FLUORIDE
GERMAN EMULSION
HYDROXAMIC ACIDS
SODIUM HYDROXIDE SOLUTION
DIMETHYLSULFOXIDE
MACROCYCLIC ETHERS
PROPIONYL FLUORIDE
PHENOLS/CATECHOLS
CARBONATE/BICARBONATE SOLUTIONS
CHLORITE SOLUTIONS
CHLORINE DIOXIDE
NITROGEN TETROXIDE
BORON TRIFLUORIDE
OZONE
SULFUR DICHLORIDE
UV/OZONE
ULTRASONIC DECOMPOSITION
COPPER LIGANDS
VANADIUM CATALYZED HYDROLYSIS
ANTHRANILIC ACID-SILVER COMPLEXATION
MAGNESIUM HYDROXIDE IMPREGNATED ALUMINA
COMPLEXATION WITH MOLYBDENUM LIGAND
PERBORATES
MICROBIAL DEGRADATION
PERMANGANATE SOLUTIONS
ENZYME PROTEINS
SODIUM SULFIDE

PHYSICAL/EXTRACTION

SURFACTANTS
STRIPPABLE COATING
VAPOR CIRCULATION
SOLVENT CIRCULATION
SUPERCRITICAL FLUIDS
ULTRASONIC EXTRACTION

PHYSICAL/ABRASIVE

HYDROBLASTING
ACID ETCH
SANDBLASTING
DEMOLITION
VACU-BLASTING
CRYOGENICS
SCARIFICATION
ELECTROPOLISHING
DRILL AND SPALL

THERMAL

FLASHBLASTING
HOT PLASMA
MICROWAVE HEATING
FLAMING
HOT GASES
SOLVENT SOAK/BURN
INFRARED HEATING
CARBON DIOXIDE LASER
ELECTRICAL RESISTANCE CONTACT HEATING

A) Mixture of 70 weight percent diethylenetriamine, 28 weight percent methyl cellosolve and 2 weight percent sodium hydroxide.

B) Mixture of 55 volume percent monoethanolamine, 45 volume percent propylene glycol and 2.5 weight percent lithium hydroxide.

C) Mixture of 54 weight percent monoethanolamine, 44 weight percent isopropanolamine and 2.5 weight percent lithium hydroxide.

phase laboratory studies. The most promising concepts recommended for further evaluation in Phase 2 were the use of:

- Hot gases
- Steam
- N-Octyl-pyridinium 4-aldoxime bromide (OPAB)
- Monoethanolamine (MEA)
- FREON 113® Vapor Circulation
- Ammonia Gas or Ammonia/Steam
- Flashblast

These suggested decontamination methods are briefly described as follows.

Hot Gases. The interior of a building is heated by hot exhaust gases from a combustion device located outside the building. As the material temperature increases, agents will decompose by pyrolysis and/or volatilize from the surface. The interior of the building will be heated by conduction. If agent volatilization occurs, provision to treat the building exhaust gas to remove/destroy the intact agent would be required.

Steam. A boiler is provided outside the building and steam is piped into the structure, decontaminating the entire building at once. The elevated temperature will promote agent hydrolysis reactions and cause volatilization of agents from subsurfaces. The steam itself should penetrate concrete, perhaps more readily than might be expected for liquid reactants. The condensate must be considered hazardous until proven otherwise.

OPAB. OPAB is a dilute aqueous solution of 1-octylpyridinium 4-aldoxime bromide. The reaction of oximes with the nerve agents is well documented, but this reagent appears to be especially effective with VX. Its safety has been validated and, in fact, it is closely related in structure to the nerve agent antidotes, PAM and toxogonin. The products produced with OPAB and nerve agents are the same as those produced on hydrolysis, but this reagent is especially appealing because of its speed and safety.

MEA. MEA is known to be a very active reagent for HD. It is good solvent for HD and is rapidly alkylated by HD. Unlike HD, the products of HD decomposition by this reagent are all water soluble (as is MEA), thus facilitating removal of products via a water wash. Once reaction with HD has taken place, it should not be reversible.

FREON 113 Vapor Circulation. FREON 113 is heated to its boiling point and the vapors allowed to circulate in a building. The vapors permeate porous building materials where they condense, solubilize the agent, and aid diffusion. The condensed FREON, laden with contaminant, is collected in a sump and treated to permit recycle.

Ammonia Gas. The appeal of gaseous decomposition systems is their ability to permeate throughout a building including subsurfaces. Ammonia should react with HD to produce thiomorpholines. Ammonia alone is not expected to effectively decontaminate nerve agents, but, in the presence of water (perhaps as steam), will raise the pH and promote hydrolytic decomposition. Because ammonia is moderately toxic, it can be introduced into a sealed building and exhausted through an absorber. This approach is thus similar to steam treatment, but provides a reagent specific for HD which will at the same time promote base catalyzed GB and VX hydrolysis in the presence of moisture.

Flashblast. The flashblast device consists of a high intensity Xenon-quartz strobe light which can be focused onto a contaminated surface. The high energy light pulse produces enough heat to remove paint and rust films and to thermally decompose surface contaminants.

1.2 Background of Phase 2 - Laboratory Evaluation

The second phase effort was designed to experimentally evaluate the concepts selected from Phase 1 and to recommend one to three of the most promising concepts for field evaluation in Phase 3. The ideal case was development of a single decontamination method which is both cost effective

and universally applicable to all types of agent-contaminated materials. However, the development of a single decontamination method specific to one agent would also be considered in the event that a "universal" concept was infeasible. Materials of concern identified from Phase 1 site surveys for which decontamination methods were to be developed in Phase 2 included:

- Stainless steel - painted and unpainted
- Mild steel - painted and unpainted
- Concrete - painted and unpainted

The approach used to develop the decontamination concepts through experimental evaluation focused on subjecting the concepts to conditions/ materials progressively more difficult to decontaminate. At each stage of the process, attempts were made to make the concept work by either altering process parameters or the use of additives. A logic plan detailing the stages of the concept development process is illustrated in Figure 2 and discussed as follows.

In the first stage of the evaluation, the decontamination effectiveness of each chemical concept (i.e., MEA, OPAB, Steam, and Ammonia) against HD, GB, and VX was determined in laboratory glassware (i.e., no matrix present). Based on these experiments the most promising concepts were selected for further evaluations. If in these tests, conditions could not be found in which an agent(s) was effectively decomposed by any one chemical concept, then an alternative replacement concept would be selected from the Phase 1 concept list and its effectiveness determined in the same manner.

In the second stage of the evaluation process, the selected chemical concepts as well as the hot gas, flashblast and vapor circulation concepts were evaluated in a test chamber. Unpainted stainless steel spiked with HD, GB, or VX was selected as the substrate for the second screening of the concepts. Unpainted stainless steel allowed the highest recovery of agent and therefore yielded the most accurate measure of decontamination effectiveness. Based on the experimental data, the three most promising concepts were then selected.

The third stage of the evaluations focused on the decontamination of painted and unpainted mild steel, painted stainless steel and concrete

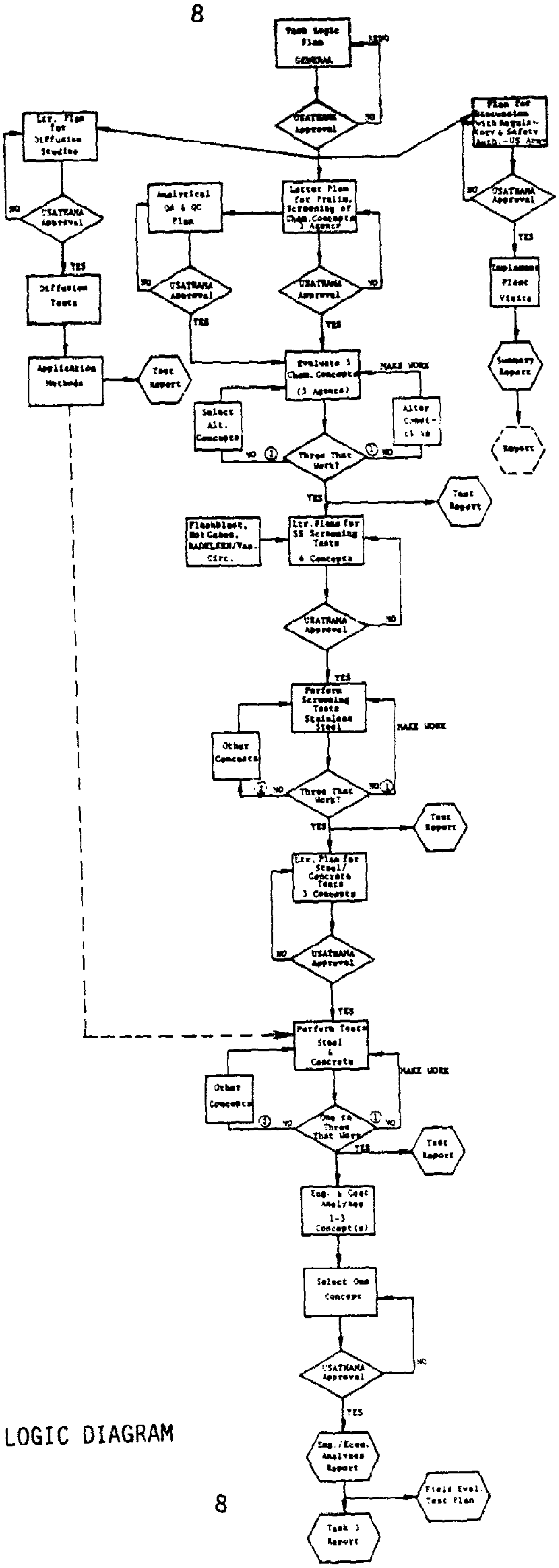


FIGURE 2. TASK 3 LOGIC DIAGRAM

in the test chamber. The materials provided places into which agent can be absorbed (i.e., paint and concrete pores). Two concepts were then selected for evaluation in the engineering/economic analyses from which a concept applicable to all three agents was recommended.

2.0 OBJECTIVES

The purpose of Phase 2 was to validate novel cost effective decontamination concepts selected in Phase 1 for the decontamination of agent contaminated facilities. The objective was to demonstrate the applicability of the selected concepts for decontamination of building materials to concentrations below the detection limit using samples that have been contaminated in a controlled manner in a laboratory environment. Data on their effectiveness, reliability, waste product characteristics, possible hazards and approximate cost were used to make a selection of the most cost-effective method for pilot testing in the subsequent phase and for detailed concept design for field trials.

3.0 SYNOPSIS OF PHASE 2 RESULTS

The Phase 2 experimental program was divided into subtasks as follows (See the Design Plan in Appendix I).

Subtask 1. Regulatory/Agency Visits
Subtask 2. Test Preparations
Subtask 3. Chemical Concept Prescreening
Subtask 4. Diffusion Studies
Subtask 5. Stainless Steel Surface Screening
Subtask 6. Steel/Concrete Tests
Subtask 7. Engineering/Economic Analysis
Subtask 8. Preparation of Final Report and Field Test Plan
Subtask 9. Fate of Agent in Concrete*
Subtask 10. JACADS Decontaminations Evaluation*
-- Analytical Summary Report*

* Additional efforts requested by USATHAMA in contract modifications.

The subtasks are summarized as follows. Detailed descriptions of the experimental and engineering efforts are given in the appendices.

3.1 Regulatory/Agency Visits

Program overviews were given and issues (e.g., 5X decontamination versus decontamination to below the detectable limit) were raised at presentations to various safety and regulatory groups. The presentations served to acquaint the DOD safety community of near-term future plans for facility decontamination methods. An initial safety agency presentation was conducted at U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) on November 2, 1983, to brief the USATHAMA Safety Group. Other briefings were given at the U.S. Army Pollution Abatement Symposium (November 6-8, 1984) held at Blacksburg, Virginia and the 21st DOD Explosives Safety Seminar (August 28-30, 1984) held at Houston, Texas.[2]

3.2 Test Preparations

A test chamber was designed and constructed such that application of a decontamination concept could be performed in a controlled environment. Design criteria for the test chamber include

- access ports to allow introduction of coupons and removal of effluents,
- allow decontamination of coupons by liquid decontaminants/ solvents, by gaseous decontaminants/solvents, and by thermal methods,
- be sized to fit within a toxic materials laboratory hood.

A detailed description of the test chamber is given in the Subtask 5 test report (See Appendix IV).

3.3 Chemical Decontamination Concept Prescreening

A preliminary evaluation of the five chemical decontamination concepts identified in Phase 1 of the Novel Processing Program was performed

in Subtask 3. The concepts which were evaluated in laboratory scale glassware included monoethanolamine (neat and 50 percent aqueous solution), aqueous solution of 1-octylpyridinium 4-aldoxime bromide (OPAB), anhydrous ammonia, steam, and steam/ammonia.

The results indicated that all of the chemical decontaminants were effective on specific chemical agents. The most promising concepts, involving the use of either steam or OPAB, achieved high destruction efficiencies (i.e. 99.5 to the detection limit of 99.8 percent destruction) for all three agents (HD, GB, and VX). Product identification results indicated that both OPAB and steam caused hydrolysis of the agent molecule whereby key bonds on the molecule (e.g., P-F on GB, P-S on VX, and C-Cl on HD) were broken. As such, Battelle and USATHAMA selected the steam and the OPAB concepts for further evaluation in subsequent subtasks involving decontamination of steel and concrete matrices. Because of the effectiveness of the other chemical decontaminants, no concept was eliminated but rather, all remaining concepts were retained in the event that an alternative decontaminant would be required in the subsequent efforts.

Detailed experimental results and mass spectra obtained from the chemical concept prescreening studies are given in Appendix II.

3.4 Diffusion Studies

Because facility decontamination includes decontamination of trace quantitites of agents which have penetrated into porous materials such as concrete, an evaluation criterion was incorporated in Phase 1 evaluations which focused on the anticipated depth of penetration of the decontaminant into porous materials. It was assumed that the depth of penetration of chemical decontaminants would be less than 1/8 inch for liquids and more than 1/8 inch (but less than complete penetration) for gases. It was recognized that an experimental effort would be required to substantiate these assumed penetration depths.

The ability for liquid and gaseous decontaminants to penetrate mortar was investigated in Subtask 4. Aqueous solutions and FREON® 113 were applied to mortar coupons by spraying and by a constant contact method.

The diffusion rate of gaseous ammonia (a candidate agent decontaminant) through mortar was determined.

Experimental results indicated spraying is the preferred method for application of aqueous based decontaminants to concrete. However, application of FREON® 113 to concrete does not appear feasible. Penetration depths of 1/4 to 1 inch were achieved by aqueous solutions applied with the spraying method. Operating parameters were determined for further evaluation of the spraying method in subsequent subtasks (5, 6 and 7) of both Task 3 (agents) and in a related effort focusing on explosive decontamination.

Gaseous ammonia was demonstrated to readily penetrate one inch thick mortar coupons. Detailed experimental results from the diffusion studies are given in Appendix III.

3.5 Stainless Steel Surface Decontamination Screening

Five decontamination concepts (steam, OPAB, hot gases, vapor, circulation, and flashblasting) were evaluated for their decontamination effectiveness of agent contaminated unpainted stainless steel surfaces. The results indicated that steam, hot gases, and OPAB are the most promising concepts. The steam and hot gases concepts decontaminated the stainless steel contaminated with HD, GB, or VX to below the detectable limit. The detectable limit for the stainless steel decontamination tests was equivalent to a 99.9 percent agent decontamination efficiency for an initial spike level of 1.2 mg agent/m^2 of surface area. Mass spectral analyses confirmed that neither agents nor agent decomposition products remained on the stainless steel surfaces following application of the hot gas decontamination concept.

The OPAB concept decontaminated stainless steel to below the detectable limit when GB was the contaminant. Results suggested that a similar decontamination effectiveness could be achieved with OPAB when either HD or VX is the contaminant. As such, Battelle and USATHAMA selected the steam, OPAB, and hot gases concepts for further evaluations in Subtask 6. Detailed experimental results from the stainless steel screening tests are given in Appendix IV.

3.6 Steel/Concrete Decontamination Tests

The steam, hot gas, and OPAB decontamination concepts were evaluated for their effectiveness in decontaminating painted mild steel, unpainted mild steel, painted stainless steel, concrete, and unglazed porcelain* coupons contaminated with HD, GB, or VX. The detectable limit for the Subtask 6 steel tests was equivalent to a 99.9 to 99.999 percent agent decontamination efficiency for an initial dose level of 1.2 mg agent/m^2. A similar decontamination efficiency was observable in the concrete and unglazed porcelain tests for an initial dose level of 1.8 mg agent/g of material.

Results of the hot gas experiments indicated that painted and unpainted mild and stainless steels, unpainted concrete and unglazed porcelain can be decontaminated to below the detectable limit by maintaining the material at a temperature of 150 C for 60 minutes when either HD, GB, or VX are the contaminant. Because undecomposed agent was volatilized from the coupons during the process, a method to remove or to decompose agent contained in the exhausted gas from a building must be defined.

Results of the steam experiments indicated that painted and unpainted mild and stainless steels, unpainted concrete and unglazed porcelain can be decontaminated to below the detectable limit by maintaining the material at a temperature near the boiling point of water for either 60 minutes when either HD or GB are the contaminants or for 240 minutes when VX is the contaminant. Because undecomposed agent was volatilized from the coupons during the process, a method to remove or to decompose agent contained in the exhausted steam and condensate from a building must be defined. One such method is to recycle the condensate through the steam generator. Experimental data indicated that boiling of contaminated condensate from the process resulted in the destruction of the residual agent.

Results of the OPAB experiments indicated that painted and unpainted mild and stainless steel can be decontaminated by applying about 15 to 30 liters/m^2 OPAB solution when HD is the contaminant and about 25 to 45 liters/

* Unglazed porcelain was selected as an inert alternative to concrete for GB and VX tests (See Appendix V and VII).

m^2 of OPAB solution when either GB or VX is the contaminant. Results of the concrete and unglazed porcelain tests indicated that VX contaminated unglazed porcelain can be decontaminated to below the detectable limit by spraying with OPAB solution. Decontamination of either HD contaminated concrete or GB contaminated unglazed porcelain to near the detectable limit by spraying with OPAB solution was also achieved. The data from these decontamination tests and the diffusion studies (See Section 3.4) indicate that the effectiveness of OPAB for decontamination of porous materials such as concrete is limited to a penetration depth of about 1/8 to 1/4 inch.

Based on the experimental evaluations, Battelle and USATHAMA selected the steam and the hot gas concepts for further evaluations in the subsequent engineering/economic analysis subtask (Subtask 7). OPAB was not selected for the engineering analyses because of its limited ability to penetrate porous materials. However, specific applications for OPAB were identified including use as a decontaminant for pipes, pumps, tanks, and other equipment and as a protective coating for external building surfaces during either hot gas or steam decontamination.

In conjunction with the decontamination tests, an air sampling method employing heated air for extraction (i.e., volatilization) of residual agent from decontaminated coupons was evaluated. Results from the heated air extractions were compared with results obtained using a solvent (e.g., hexane or methylene chloride) extraction method on similar samples. The results indicated that the solvent extraction method is more reliable in terms of specificity to the agents and more effective at extracting agent than the air sampling method.

Detailed experimental results from the steel/concrete tests are given in Appendix V.

3.7 Engineering/Economic Analyses

An engineering/economic analysis was performed on the hot gas and steam decontamination concepts selected from the experimental evaluations in Subtask 6. Equipment was specified and costs were estimated for application of the concepts to a model facility representative of structures observed

during the Phase 1 site surveys. Results of the analyses suggest that it is feasible to apply the hot gas and steam contamination concepts for decontamination of field structures. In terms of cost, the hot gas concept is slightly preferred over the steam concept for the assumption that the entire building is contaminated throughout. In the hot gas concept, flue gases from the combustion of oil or natural gas are directed into a sealed and insulated building. Gas exhausted from the building is treated in an afterburner to destroy traces of volatilized agent, cooled by quenching with water, directed through an induced draft fan, and exhausted to the outside from a stack. The induced draft fan maintains both a flow through the system and a slight negative pressure within the building to minimize leakage of air potentially contaminated with agent to the outside. A detailed discussuion of the results of the analyses is given in Appendix VI.

3.8 Fate of Agent in Concrete

Suitable analytical methods for the agent decontamination studies were unavailable when laboratory experiments were being initiated. Consequently, analytical method development was undertaken for the agents GB, HD, and VX on selected building materials. Building materials examined included painted and unpainted mild steel, stainless steel, and concrete. Attempts to recover agents by solvent extraction from the painted and unpainted steels were successful and produced no unanticipated results. Use of the solvent extraction method proved significantly less successful for agents added to concrete than was observed for agents on metal. Assorted modifications to this basic method were tried but the results were disappointing, in that GB could not be extracted by any technique attempted at levels significantly above the method detection limit. Although HD and VX could be partially recoved from unpainted concrete, the precision (repeatability) observed was extremely poor. These results suggested that all or part of the agent applied to the concrete specimen was not available to be extracted due to interaction with the concrete. Results of the analyses suggest that the interaction of the nerve agents with concrete is a chemical

reaction which causes agent hydrolysis. The interaction of concrete with HD appears to be incomplete or reversible in that substantial amounts of HD are extractable even after a 24 hour exposure period.

A detailed discussion of the results on the fate of agent in concrete studies is given in Appendix VII.

3.9 JACADS Decontaminants Evaluation

In support of routine decontamination anticipated during operations at the JACADS facility, the JACADS experimental study evaluated the ability of three candidate chemical decontaminants to decontaminate specific unpainted and painted steel surfaces representative of construction materials selected for the JACADS design. Solutions of 10 percent Na_2CO_3 and 1 percent NaOH were separately tested to decontaminate steel coupons spiked with GB. A 5 percent commercial NaOCl solution was tested to decontaminate VX and HD. Following decontamination, the coupons, spent decontamination solution and chamber rinses were analyzed for residual agent. Results suggested that the JACADS decontaminants are effective in that the coupons were decontaminated to either below the detectable limit or to low levels of residual agent.

A detailed discussion of the results on the JACADS study is given in Appendix VIII.

3.10 Summary of Analytical Methodology in Support of Task 3

At the request of USATHAMA, a summary report detailing the analytical methodology used in support of Task 3 was prepared and is given in Appendix IX. The analytical method developments indicate the utility of the extraction/GC-FPD method of analysis for determining residual HD, GB, or VX in or on matrices found in agent contaminated structures. It has been used instead of the air sampling-impinger method accepted by the Army. The extraction procedure proved to be rapid and was reliable enough to demonstrate the effectiveness of various substrate decontamination concepts.

4.0 CONCLUSIONS/RECOMMENDATIONS

The concept selection results from the Phase 2 experimental and engineering subtasks are illustrated in Figure 3. The experimental evaluations (Subtasks 3, 4, 5 and 6) demonstrated that the hot gas, steam and OPAB concepts were effective decontaminants for each agent/material combination investigated. Each of the other decontaminants (e.g., flashblast, ammonia, etc.) was effective to some extent, but either the effectiveness was limited to specific agent/material combinations or the concept appeared less promising.

The engineering evaluations indicated that it is feasible to apply either the hot gases or the steam decontamination concept to structures representative of Army installations. Because of the limited depth of penetration into porous materials, the use of OPAB as a general decontaminant is not feasible. However, OPAB is recommended for use as a protective coating during application of the hot gas or steam concept and as a non-corrosive decontaminant for specific applications such as decontamination of the inside of pipes, sumps, and other equipment.

Results of the economic analyses indicated that the hot gas concept is preferred over the steam concept. As such, the hot gas concept is recommended as the primary decontamination concept for field evaluation in Phase 3 of the program. Steam should be retained as a back-up concept to the hot gas concept.

Analytical method development activities demonstrated the utility of the solvent extraction/gas chromatography technique for the quantification of agent on building materials such as painted and unpainted steels. Attempts to quantitatively recover HD, GB or VX when spiked onto concrete were unsuccessful. Investigations as to the fate of agent on concrete indicated that an agent/concrete interaction, possibly a chemical reaction such as hydrolysis, is responsible for the inability to recover the spiked agents.

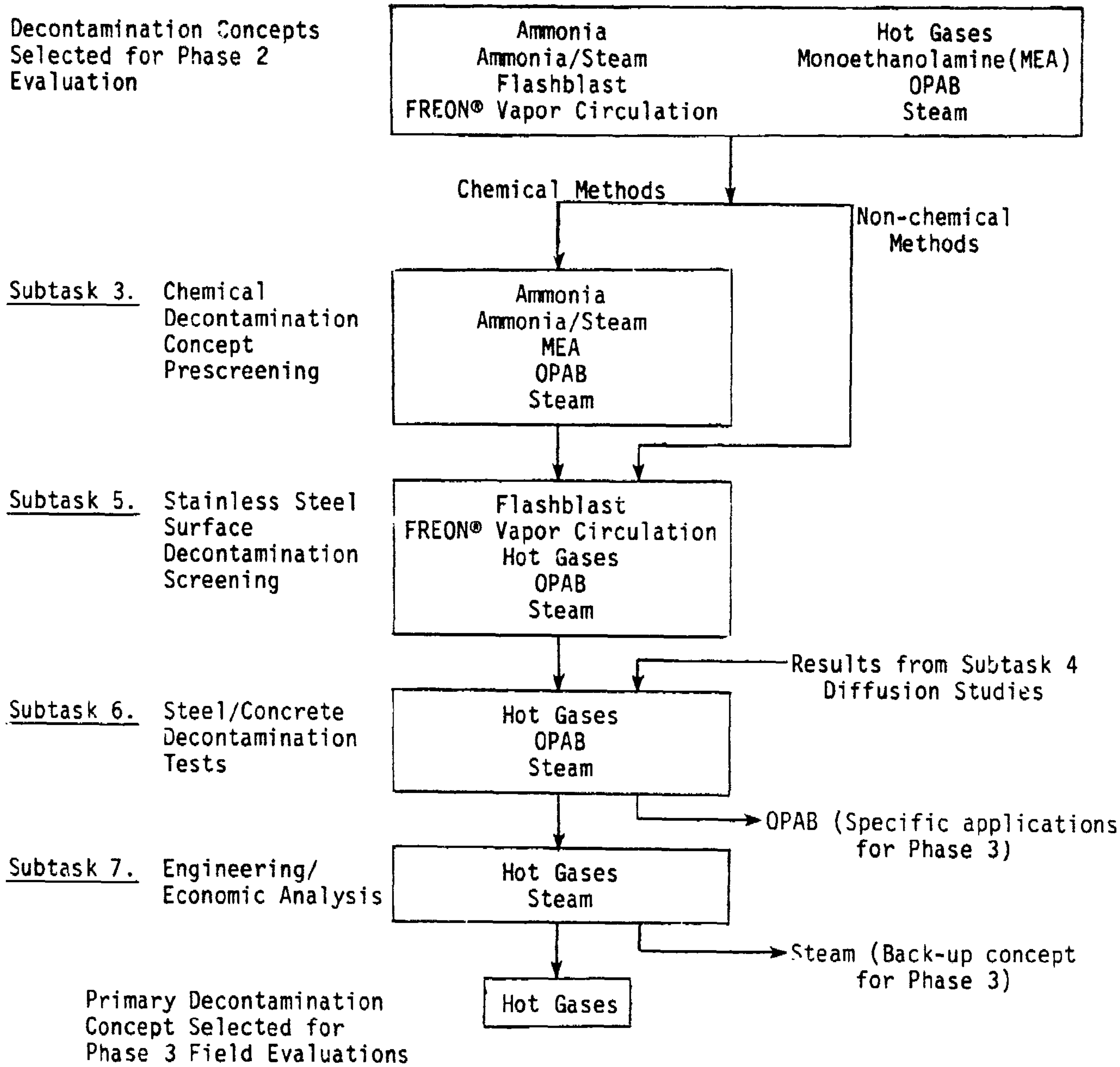


FIGURE 3. CONCEPT SELECTION RESULTS FROM THE PHASE 2 EXPERIMENTAL AND ENGINEERING EVALUATIONS

APPENDIX I

DESIGN PLAN

DESIGN PLAN

for

TASK 3

DEVELOPMENT OF NOVEL DECONTAMINATION
TECHNIQUES FOR AGENT-CONTAMINATED FACILITIES

Contract DAAK11-81-C-0101

by

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APPENDICES

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TASK 3

DEVELOPMENT OF NOVEL DECONTAMINATION TECHNIQUES FOR AGENT-CONTAMINATED FACILITIES

1.0 SUMMARY

The development of novel concepts for the decontamination of chemical agent-contaminated buildings is being carried out by Battelle Columbus Laboratories (Battelle) for the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) under Contract No. DAAK11-81-C-0101. In the previous phase (Task 1), ideas were systematically developed into concepts for decontaminating buildings and equipment. These concepts were evaluated and ranked with respect to technical and economic factors. Also, knowledge gaps relating to application of the concepts were selected for laboratory evaluation in Task 3 including five chemical concepts (OPAB, MEA, Steam, NH_3, NH_3/Steam), two thermal concepts (hot gases, flashblast) and one physical concept (RADKLEEN®/vapor circulation). Task 3 has the objectives of resolving the technical uncertainties identified in Task 1 through bench-scale experiments and refining the technical/economic analyses of the most promising concepts.

Task 3 is broken into eight technical subtasks covering (1) a resource/work plan, (2) test preparations, (3) chemical concept prescreening, (4) diffusion studies, (5) surface decontamination, (6) surface/subsurface decontamination, (7) engineering/economic analyses, and (8) report/field test plan.

2.0 BACKGROUND

Decontamination of previously utilized chemical agent manufacturing and testing facilities is necessary to allow the Department of the Army to restore the facilities for alternate use or to dispose of them in excessing actions. Included in the facilities are the building structures, sumps, processing equipment, underground and above-ground storage tanks, and associated transfer systems. Facility decontamination involves not only the decontamination of exposed surfaces but also the decontamination of trace quantities of

agents which may have penetrated into the material through pores, cracks, or other openings.

Materials of concern identified from Task 1 site surveys for which decontamination methods are to be developed in Task 3 include:

- stainless steel - painted and unpainted
- mild steel - painted and unpainted
- concrete - painted and unpainted

3.0 OBJECTIVES

The objectives of this task are to:

- experimentally evaluate the concepts selected in Task 1 for decontamination effectiveness on various materials,
- perform an engineering/economic analysis on the most promising concepts selected from the experimental effort,
- identify remaining knowledge gaps associated with the most viable concept(s) and prepare a test plan to resolve the knowledge gaps through implementation of the concept at a field site.

4.0 TECHNICAL APPROACH

Task 3 efforts are divided into eight technical subtasks as shown in the work breakdown structure (WBS) illustrated in Figure 1. The objectives and technical approaches to be used in each subtask are described below.

4.1 Subtask 1. Resource/Work Plan

The objectives of this subtask are to (1) provide an overall plan for the task (this document) and to (2) review government regulatory and safety requirements relating to agents and agent decontamination.

TASK 3

LABORATORY EVALUATION OF

AGENT DECONTAMINATION CONCEPTS

1.0 Resource/Work Plan

- 1.1 Design Plan
  - 1.1.1 USATHAMA Approval
- 1.2 Regulatory/Safety Agency Review Plan
  - 1.2.1 USATHAMA Approval
- 1.3 Agency Visits
- 1.4 Regulatory/Safety Findings Report

2.0 Test Preparations

- 2.1 Chamber Design
- 2.2 Chamber Operation Test Plan
  - 2.2.1 USATHAMA Approval
- 2.3 Chamber Construction/Performance Tests
- 2.4 Analytical QA & QC Plan
  - 2.4.1 USATHAMA Approval
- 2.5 Coupon Preparation

3.0 Chemical Concept Prescreening

- 3.1 Test Plan
  - 3.1.1 USATHAMA Approval
- 3.2 Chemical Prescreening Tests
- 3.3 Test Report (Select 1-3 concepts)
  - 3.3.1 USATHAMA Approval

4.0 Diffusion Studies

- 4.1 Test Plan
  - 4.1.1 USATHAMA Approval
- 4.2 Diffusion Calculations
- 4.3 Diffusion Tests
- 4.4 Diffusion Test Report
  - 4.4.1 USATHAMA Approval

FIGURE 1. WORK BREAKDOWN STRUCTURE TASK 3

TASK 3, CONTINUED

5.0 Stainless Steel Surface Screening

- 5.1 Flashblast/Hot Gases/Vapor Circ. - RADKLEEN Test Plan
  - 5.1.1 USATHAMA Approval
- 5.2 Flashblast/Hot Gases/Vapor Circ. - RADKLEEN Tests
- 5.3 Chemical Concept(s) Test Plan
  - 5.3.1 USATHAMA Approval
- 5.4 Chemical Concept(s) Tests
- 5.5 Test Report
  - 5.5.1 USATHAMA Approval

6.0 Steel/Concrete Tests

- 6.1 Test Plan
  - 6.1.1 USATHAMA Approval
- 6.2 Testing S.S./C.S./Concrete - with and without paint
- 6.3 Test Report (Select 1-3 concepts)
  - 6.3.1 USATHAMA Approval

7.0 Engineering/Economic Analysis

- 7.1 Engineering Analysis
- 7.2 Economic Analysis
- 7.3 Knowledge Gap Identification
- 7.4 Analysis Report (Recommend one concept)
  - 7.4.1 USATHAMA Approval

8.0 Field Test Plan/Task 3 Report

- 8.1 Task 3 Report (Draft)
  - 8.1.1 USATHAMA Approval
- 8.2 Field Test Plan
  - 8.2.1 USATHAMA Approval

FIGURE 1, continued

Safety regulations which will be reviewed include DARCOM Safety Regulation 385-31 (HD) and DARCOM-R 385-102 (GB and VX). Information from these and other pertinent documents will be used to prepare a regulatory/safety agency review plan which consists of a letter recommending the agencies to be visited and the topics to be discussed. Tentatively scheduled for visits are agencies such as Department of Defense Explosion Safety Board and safety offices at agent manufacturing/demilitarization sites such as Rocky Mountain Arsenal and Tooele Army Depot. Included in the discussion topics will be the question of "5X" decontamination, defined as thermal treatment at 1000 F for 15 minutes, versus decontamination to below the detectable limit by chemical, physical, or milder thermal methods.

4.2 Subtask 2. Test Preparations

The objectives of this subtask are to (1) design, construct, and evaluate a test chamber, (2) develop a Quality Assurance and Quality Control (QA/QC) Plan, and (3) prepare coupons of the materials used in the chamber tests.

The test chamber will be designed and constructed such that application of a decontamination concept may be performed in a controlled environment. A chamber operation test plan which will include design drawings of the chamber and operating scenarios will be submitted for USATHAMA approval. Design criteria for the test chamber will include:

- access ports to allow introduction of coupons and removal of effluents,
- allow decontamination of coupons by liquid decontaminants/solvents, by gaseous decontaminants/solvents, and by thermal methods,
- be sized to fit within a toxic materials laboratory hood.

A QA/QC plan will be prepared based on guidance to be received from USATHAMA. The plan will be submitted for USATHAMA approval.

Painted and unpainted coupons of stainless steel, concrete, and carbon steel will be prepared in this subtask for subsequent use in diffusion and chamber decontamination experiments. The coupons will be uniformly sized to allow direct comparison of results obtained from the experiments.

4.3 Subtask 3. Chemical Concept Prescreening

The objective of this subtask is to experimentally evaluate the five chemical concepts in terms of reaction kinetics and decontamination effectiveness. The five chemical concepts include:

- OPAB (1-Octylpyridinium-4-aldoxime bromide) in an aqueous solution containing a surfactant
- MEA (monoethanolamine) in an aqueous solution or undiluted
- Steam
- NH_3 (anhydrous)
- Steam/NH_3

Each concept will be evaluated under a variety of conditions in an attempt to determine the optimum operating conditions that will sufficiently decompose each of the three agents (GB, HD, and VX). A letter test plan detailing the methodology, parameters to be investigated (e.g., time, temperature, decontaminant concentration), and analytical techniques will be submitted for USATHAMA approval.

The experiments will be performed in laboratory glassware in which known quantities of neat agent will be contacted with an excess of decontaminant. The mixture will then be periodically sampled and analyzed for residual agent. Analytical techniques will be refined, as required, to permit quantitative detection of agent in the presence of the decontaminants and the decomposition products. If conditions cannot be found in which an agent(s) is effectively decomposed by any one chemical concept, then an alternative replacement concept will be selected with USATHAMA approval and its effectiveness determined in the same manner.

Based on the experimental results, a maximum of three chemical concepts will be selected for further evaluation in Subtask 5. A test report detailing the test results and the selected concepts will be submitted for USATHAMA approval.

4.4 Subtask 4. Diffusion Studies

The overall effectiveness of a chemical or solvent decontamination concept is dependent upon the ability of the decontaminant to penetrate into (and in the case of a solvent, out of) porous materials into which agents may have penetrated. The objective of Subtask 4 is to determine the conditions which will allow optimum penetration of chemical or solvent decontaminant into a porous material, i.e., concrete.

The decontaminants to be investigated in this subtask include:

- Aqueous solutions containing surfactants
- MEA
- Gaseous NH_3 (anhydrous)
- Freon® solvent

Since these decontaminants/solvents are representative of the chemical and physical decontamination concepts for both agents and explosives, the results of this subtask will be utilized in both Task 3 (agents) and Task 4 (explosives).

Aqueous solutions, MEA, Freon®, and similar liquids will be applied to concrete coupons by spraying. Spray pressure, the time the spray is maintained on the coupon, and the number of spray applications will be varied to determine optimum application times to be used for subsequent chamber tests. Surfactants (e.g., Triton X-100®) will also be added, if necessary, to enhance the penetration of aqueous solutions into concrete.

The diffusion rate of gaseous NH_3 through concrete coupons will be determined experimentally by exposing one side of a concrete coupon to NH_3 and measuring the concentration of NH_3 with time on the opposite side of the coupon.

A letter test plan detailing the planned liquid and gas diffusion experiments will be submitted to USATHAMA for approval. During the two- to three-week period required for approval, calculations will be performed to estimate the depths the various decontaminants will penetrate into concrete. A literature search will also be performed to determine a range of values for various physical properties of concrete, i.e., porosity, pore sizes, etc., which will be used in these calculations. The calculations will be used to determine initial operating parameters for the diffusion experiments and may allow correlations to be developed indicating the effective penetration of decontaminants in various types of concrete.

A test report summarizing the diffusion test results, calculations, and proposed operating conditions for decontaminant application to concrete will be submitted for USATHAMA approval.

4.5 Subtask 5. Stainless Steel Surface Screening

In this subtask, the most promising chemical concepts from Subtask 3 (maximum of three concepts), as well as hot gases, flashblast, and vapor circulation/RADKLEEN^{R} concepts will be evaluated in a test chamber. Unpainted stainless steel (S.S.) coupons spiked with HD, GB, or VX will be used as the test substrate. S.S. coupons were selected as the first test substrate since it is the substrate from which analytical techniques achieve the highest recoveries of agent and therefore yield the most accurate measure of decontamination effectiveness. Also in this subtask, waste products from the treatment will be characterized, reaction kinetics determined, and analytical performance verified.

Two test plans covering this subtask will be submitted for USATHAMA approval. One test plan covering the hot gases, flashblast, and vapor/circulation concepts which will not be prescreened will be submitted. Following selection of the most promising chemical concepts from Subtask 3, a second test plan (chemical concepts) will be submitted. By submitting two test plans, work may proceed while the Subtask 3 test results are being evaluated.

The experimental data will be analyzed and the three (maximum) most promising concepts selected for further evaluation in Subtask 6. If, however, the data indicate that none of the concepts effectively decontaminates stainless steel coupons spiked with a particular agent(s), a replacement concept will be selected with the concurrence of USATHAMA and its effectiveness determined in the same manner. A test report summarizing the results of Subtask 5 will be submitted for USATHAMA approval.

4.6 Subtask 6. Steel/Concrete Tests

Subtask 6 represents the final test series in Task 3. In this subtask, the three most promising concepts from Subtask 5 will be thoroughly evaluated based on decontamination effectiveness, reaction kinetics, analytical performance, and waste product formation. Substrates to be investigated will include coupons of stainless steel (painted and unpainted), carbon steel (painted and unpainted), and concrete (painted and unpainted) spiked with HD, GB, or VX. Results from the diffusion studies (Subtask 4) will be used to specify initial conditions for application of liquid and/or gaseous decontaminants to the concrete coupons. Decontamination versus depth of penetration into this porous substrate will be investigated. A letter test plan detailing this experimental effort will be submitted for USATHAMA approval.

Experimental results will be analyzed and the best one to three concepts will be selected for evaluation in Subtask 7. A Subtask 6 test report will be submitted for USATHAMA approval.

4.7 Subtask 7. Engineering/Economic Analysis

A detailed engineering/economic analysis will be performed on the concepts selected in Subtask 6. The engineering analysis will utilize experimental data obtained in the previous subtasks to specify a decontamination process. The process will then be costed based on decontamination of the model facility defined in Task 1.

The experimental data which will serve as the basis for the analyses includes:

- Reaction kinetics
- Heat requirements
- Solvent/decontaminant requirements
- Waste product characterization
- Application methods, e.g., spraying times, number of applications, etc.

From these data, the following will be specified:

- Process flowsheets
- Process equipment
- Waste disposal requirements
- Building preparation/clean-up requirements
- Operation schedule (set-up, application, and equipment tear-down times)
- Safety requirements (potential hazards and protective methods)

Knowledge gaps that remain following the above analysis will then be identified.

Next, an economic analysis will be performed. The process(es) identified above will be costed based on building damage/repair costs, material/utility costs, equipment cost and manpower cost. Following this analysis, decontamination procedures which are applicable to all three agents will be recommended. USATHAMA will participate in the selection of the final concept(s). Results of the analyses will then be summarized in a final subtask report which will be submitted for USATHAMA approval.

4.8 Subtask 8. Field Test Plan/Task 3 Report

A field test plan will be prepared in Subtask 8 for (1) applying the decontamination procedure(s) identified in Subtask 7 to decontaminate Army concrete/steel structures, (2) sampling the structures for residual agent, i.e., sampling methods and types of samples, and (3) resolving the knowledge gaps identified in Subtask 7. The field test plan will be submitted for USATHAMA approval.

Included in Subtask 8 will be the submission of the Task 3 report which will summarize test results, agency discussions, and technical analyses performed in Task 3. The report will be submitted for USATHAMA approval.

4.9 Contingency Plans

As indicated in the Task 3 logic diagram illustrated in Figure 2, it may be necessary to select alternative replacement concepts during the course of the Task 3 experimental effort. Alternatives will be selected if the concept(s) remaining following the selection procedures are not applicable to all three agents and if attempts to make the concept(s) work have failed. In this case, concepts from previous subtasks will be re-examined and, if necessary, alternative concepts identified in the Task 1 efforts may be utilized. The selection of a replacement concept will be performed with USATHAMA participation.

5.0 DEVIATIONS/ADDITIONS

This design plan generally follows the government tasking document and all 32 work units have been incorporated into the eight subtasks. Deviations from the tasking document include:

- The chemical concepts will be prescreened in laboratory glassware rather than in the test chamber.
- Diffusion studies will focus on the penetration of decontaminants (not agents or simulants) into concrete.

6.0 INTERFACING

Task 3 will interface with the Task 4 efforts involving explosive decontamination. Parallel efforts in both tasks will provide in economies in chamber design, construction, and performance tests; coupon preparation; and

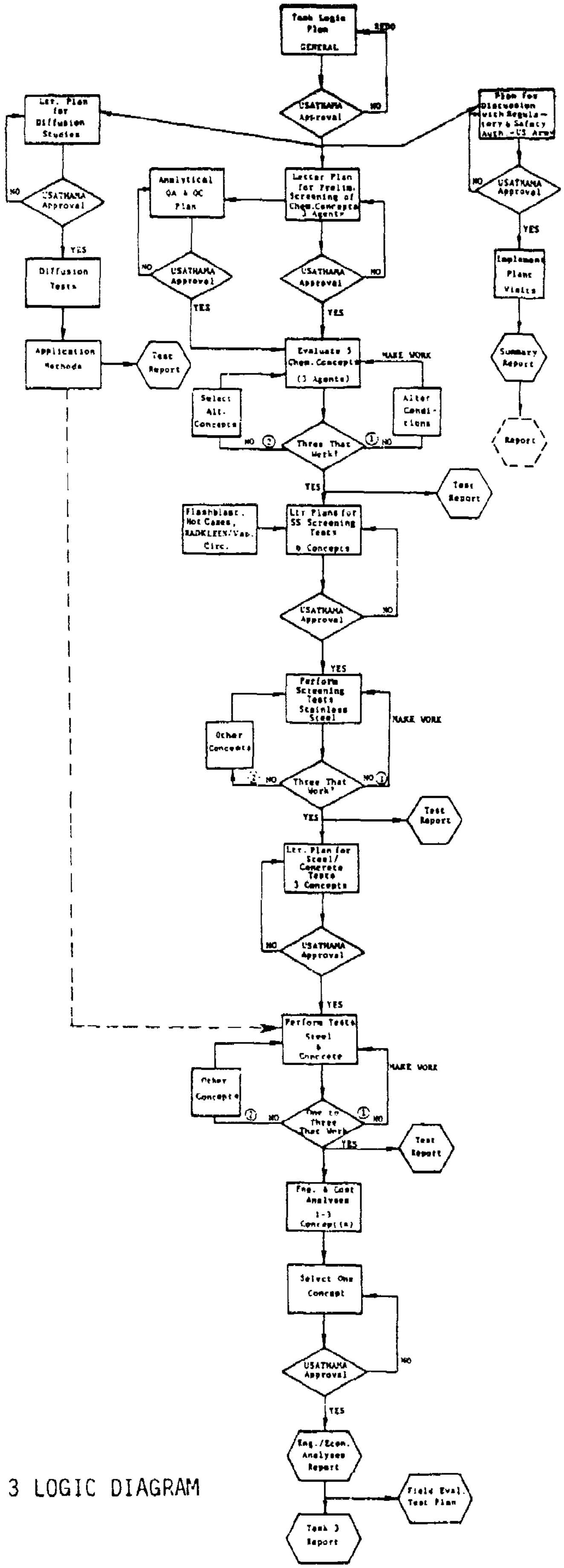


FIGURE 2. TASK 3 LOGIC DIAGRAM

engineering/economic analyses. Also, the results from the diffusion studies (Subtask 4) will be utilized by both Tasks 3 and 4 for designation of liquid/ solvent application methods.

7.0 FACILITIES

Experiments involving surety levels of agent will be performed in the Hazardous Materials Laboratory. Experiments with non-surety levels of agent will be performed in the Toxic Substances Laboratory. A brief description of these laboratories is given in Appendix B. A more complete description of the Hazardous Materials Laboratory is in the Facility Security Plan provided to USATHAMA during Task 1 efforts.

8.0 GOVERNMENT-FURNISHED PROPERTY/ASSISTANCE

The following supply of agents, in storage at the Hazardous Materials Laboratory, is currently available for Task 3 use:

HD - 13.9 ml (includes 5 ml of SARM)
GB - 13.6 ml (includes 5 ml of SARM)
VX - 18.9 ml (includes 10 ml of SARM)

It is anticipated that the above supply is sufficient to complete Task 3 experimental work.

The government will make arrangements for meetings with government regulatory/safety agencies (Subtask 1).

APPENDIX A

<u>GOVERNMENT TASKING DOCUMENT</u>

Novel Processing Technology

A. Task Order Number: 3

B. Task Order Title: Development of Novel Decontamination Techniques for Chemical Agent (GB, VX, HD) Contaminated Facilities - Phase II

C. Contract Number: DAAK11-81-C-0101

D. Background:

1. Decontamination of facilities previously utilized for chemical agent manufacture or testing is anticipated to permit the Department of the Army to restore such facilities for alternate use or to dispose of them in excessing actions. Included are not only the structures themselves but also underground and above surface storage tanks, processing equipment, sumps and associated transfer systems. Required decontamination involves exposed surfaces of the materials as well as the decontamination of trace quantities of agents which have penetrated into the materials, cracks, or other openings.

2. Materials of concern which shall require decontamination and which shall be included in this study are:

a. Stainless steel - painted and unpainted.

b. Mild steel - painted and unpainted.

c. Concrete - painted and unpainted.

3. This study follows Task 1 of this contract wherein the contractor identified potential decontamination technologies, applied selected economic and technical evaluation criteria to those technologies, rank ordered the candidates, and in conjunction with USATHAMA recommended those worthy of further laboratory evaluation in Phase II (this task). It is anticipated that at the completion of this task order effort, decontamination concepts will have been evaluated sufficiently such that recommendations can be made for pilot testing the selected concept(s).

E. Phase II Purpose and Objectives: The purpose of this task order is to validate new cost effective decontamination concepts selected in Phase I for decontamination of agent contaminated facilities. The objective is to develop sufficient information so that the final selected concept(s) can be recommended for subsequent pilot testing.

F. Statement of Work:

1. Figure 1 outlines the various work units for this task and the schedule for their implementation. This SOW is keyed to work units on Figure 1. The work to be performed on this task is based on the Task 1 effort and generally follows the recommendation of the preliminary Phase II test plan submitted under Item F.7 of that task order.

2. The first work unit after task initiation shall be preparation of the overall work plan/resource plan. This plan shall include a detailed schedule, a detailed work breakdown structure (WBS) and a resource utilization plan keyed to the WBS.

3. Work units 3 and 4 entail a review of regulatory and safety requirements and shall be performed to determine the most recent developments in these areas in order to better define decontamination levels. Germane organizations such as EPA, Department of Defense Explosives Safety Board, Department of Transportation and the DARCOM Field Safety Office shall be included. A report summarizing the findings of this study shall be prepared and submitted.

4. Also early (work unit 5) in this task order, a chamber for conducting agent testing of various concepts shall be designed, constructed and evaluated. This chamber shall be small enough to fit into a conventional fume hood, fitted with entry/exit ports for introduction and removal of samples and exhaust ports to permit sampling of out-gassed products.

5. Work units 6-10 are the preliminary screening tests of chemical concept candidates determined in Task I. These concepts include: MEA, OPAB, NH_3, steam NH_3/steam and flashblast. A letter test plan shall be submitted for USATHAMA's written concurrence before testing is begun and a letter test report shall be submitted detailing test results when concluded. Chamber tests of each concept shall be conducted and waste products and analytical performance shall be characterized. From these tests, a maximum of three concepts shall be recommended for further evaluation.

6. Work units 11-15 are for diffusion studies to evaluate penetration of agents into concrete (worst case). Agents and/or simulants shall be allowed to penetrate concreted samples which shall subsequently be sectioned, pulverized, extracted, and analyzed. These data shall be used to obtain diffusion data which shall allow assessment of penetration of agents and decontaminants into concrete over a period of time and the effects of variables such as temperature, concentration and exposure duration. These studies shall indicate appropriate application times for decontaminants. A diffusion letter test report shall be submitted detailing results of these tests.

7. Work units 16-20 are for stainless steel surface screening tests, including a letter test plan and letter test report. This test series shall include chamber tests of the three chemical concepts (from the preliminary screening) plus ~~hot gas, vapor circulation~~ and Rad-Kleen concepts; on stainless steel coupons. Waste product shall be evaluated as well as analytical performance. These tests shall provide data to select the best three concepts for evaluation in the next phase. The test report shall detail test results and the logic for selection of the three recommended concepts.

8. Work Units 21-25 detail the final evaluation testing. Each of the three concepts selected from the stainless steel surface screening tests shall be thoroughly evaluated with each of the designated materials of concern - mild steel (painted and unpainted), stainless steel (painted and unpainted), concrete (painted and unpainted). Decontamination effectiveness, waste product verification and analytical performance shall be determined. These data shall

be analyzed and shall form the basis for selection of the one (minimum) to three (maximum) final recommended decontamination methods. Details of this recommendation shall be included in the letter test report.

9. Work units 26-28 include an engineering/economic analysis of the final 1-3 concepts chosen above. Auxiliary considerations (to technical performance) shall be considered such as building repair costs, development costs, utility and fuel costs, equipment costs, material costs and labor costs. The economic analysis shall be utilized as the basis for making the selection of the final single best concept (if more than one was considered) to be field/pilot tested. USATHAMA shall participate in and approve the selection in writing.

10. Work units 29-31 are for preparation of a comprehensive final report (Contract Data Item A002). All pertinent information developed during efforts on this task order shall be compiled into a draft final report and submitted for review and approval. The final report shall be submitted within 30 days after Government approval of the draft.

11. Work unit 32 is the preparation of a recommended test plan for field evaluation of the decontamination concept selected in this task order.

12. Technical reviews shall be held as delineated in work unit 33. Four of these reviews shall be held at the contractor's facility and four shall be held at USATHAMA. Additional meetings shall be scheduled on an as required basis.

13. Analytical method development/refinement/certification shall be performed as required to support this task.

G. Testing Requirements: Analytical methods certified in accordance with the USATHAMA QC Plan shall be utilized if available. However, the actual QA/QC level shall be specified by the COR.

H. Items/Data to be Delivered:

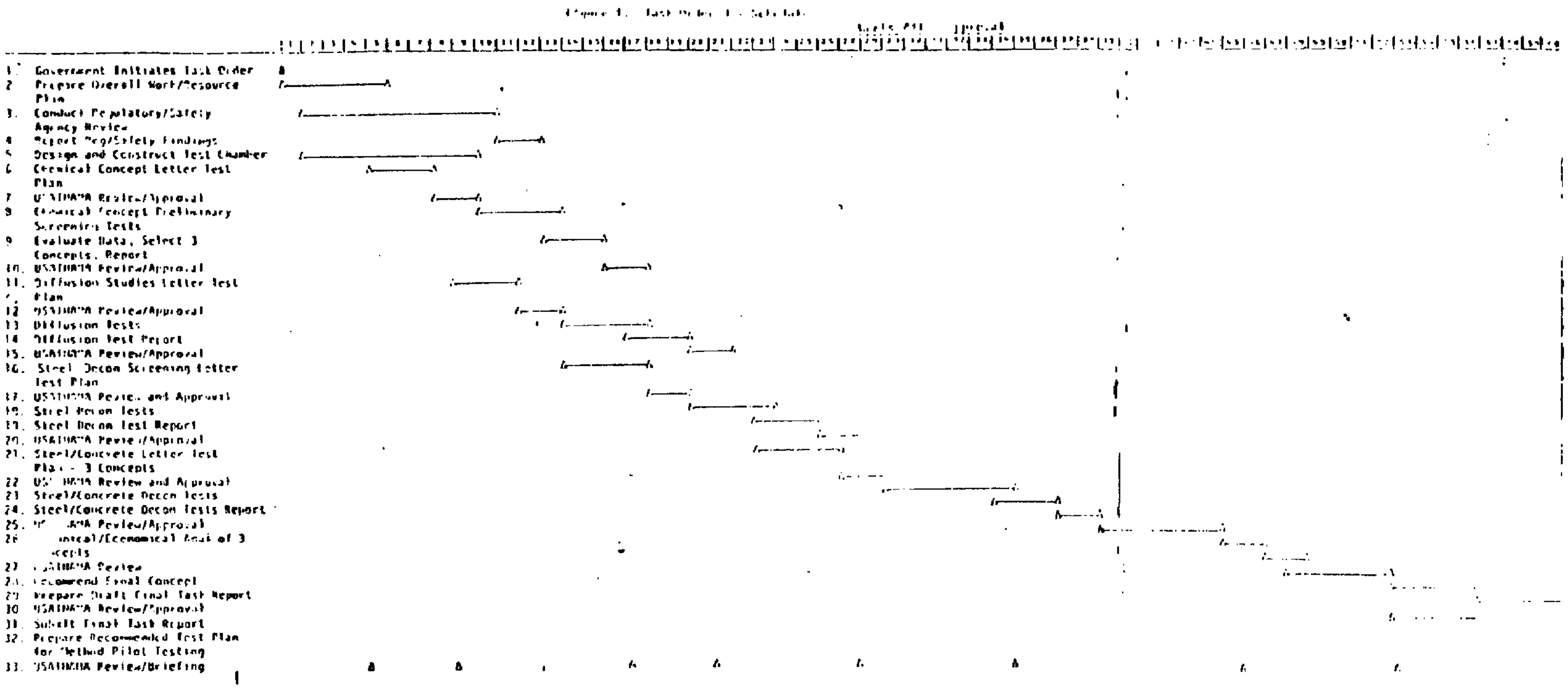
1. Letter test plans and letter test reports shall be submitted for each of the four test sequences outlined in Chart 1. (Work units 3, 6, 9, 11, 14, 16, 19, 21 and 24). Ten copies of each shall be submitted.

2. A draft technical report (10 copies) documenting the findings and recommendations of this study shall be provided to the Government 52 weeks after task initiation. The final technical report (Sequence A002 CDRL, DD Form 1423), shall be provided to the Government within 30 days after approval of the draft.

I. Government Furnished Property and/or Assistance: The Government shall make arrangements for meetings with Regulatory/Safety Government Agencies for the purpose of conducting the Regulatory/Safety Review (work unit 3).

J. Hazards Information: Information regarding safety materials used on this task order are contained in the contract.

K. Desired Period of Performance or Completion Date: Refer to Figure 1. The overall period of performance is 60 weeks.


1. Government Initiates Task Order
2. Prepare Overall Work/Resource Plan
3. Conduct Regulatory/Safety Agency Review
4. Report Reg/Safety Findings
5. Design and Construct Test Chamber
6. Chemical Concept Letter Test Plan
7. USATHAMA Review/Approval
8. Chemical Concept Preliminary Screening Tests
9. Evaluate Data, Select 3 Concepts, Report
10. USATHAMA Review/Approval
11. Diffusion Studies Letter Test Plan
12. USATHAMA Review/Approval
13. Diffusion Tests
14. Diffusion Test Report
15. USATHAMA Review/Approval
16. Steel Decon Screening Letter Test Plan
17. USATHAMA Review and Approval
18. Steel Decon Tests
19. Steel Decon Test Report
20. USATHAMA Review/Approval
21. Steel/Concrete Letter Test Plan - 3 Concepts
22. USATHAMA Review and Approval
23. Steel/Concrete Decon Tests
24. Steel/Concrete Decon Tests Report
25. USATHAMA Review/Approval
26. Technical/Economical Anal of 3 Concepts
27. USATHAMA Review
28. Recommend Final Concept
29. Prepare Draft Final Task Report
30. USATHAMA Review/Approval
31. Submit Final Task Report
32. Prepare Recommended Test Plan for Method Pilot Testing
33. USATHAMA Review/Briefing

APPENDIX B

FACILITY DESCRIPTION

Hazardous Materials Laboratory (HML)

Battelle has available a remote site hazardous materials laboratory at its West Jefferson facility. The laboratory is designed to provide all of Battelle's sponsors with a facility in which to conduct research projects using toxic and hazardous materials in a controlled, acceptable manner. A more detailed description of HML can be found in the Facility Security Plan submitted under Task 1.

The laboratory functions as both a research laboratory and as a technology development laboratory. Scientists in this laboratory are experienced in the specific needs of hazardous materials handling including decontamination, detection, alarms technology, general analysis, and evaluation of new materials. Newer technologies such as improved processes, improved analytical methods, test methods development, etc., also fall under this laboratory's activities. It is a 1,250-square foot facility, located within an existing laboratory building.

The hazardous materials laboratory has the following characteristics. The walls are 8-inch cement block; the floor and ceiling are reinforced concrete. All surfaces are painted with two coats of epoxy to create an impermeable, easy-to-wash surface.

The perimeter doors are heavy-duty hollow metal units with locks and hardware as required by security regulations with all doors except the controlled access door security-sealed. All perimeter doors are equipped with crash hardware. Door glass, windows, and perimeter openings greater than 92 square inches are security-screened with No. 9 expanded metal. A Honeywell security system, including door alarm switches and an area motion detection device, gives alarm annunciation at the site guardhouse, as does the area fire alarm system.

Stainless steel-lined fume hoods with dished work surfaces are used to keep any spills contained and to simplify clean-up. The hoods have been modified with the addition of interconnecting passthroughs. One hood has a pair of lockable storage cylinders that offers secure containment of materials in the event of a tornado.

Airflow through the laboratory comes from a separate mechanical system which supplies ventilation. The work areas are kept at negative pressure with respect to the clean areas by a pneumatic control system. All laboratory air exhausts through the hoods at 150 fpm average face velocity. A modulating damper in the exhaust ductwork compensates for changes in system static pressure and maintains constant flow. Each hood is equipped with a velocity alarm that gives an audible and visual alarm.

All exhaust air passes through a filter system consisting of a prefilter, a primary absolute, a primary charcoal, a redundant charcoal, and a final absolute filter. The filters are installed in a welded steel, bagout-type housing with sampling ports, static pressure ports, and isolation dampers to allow filter changes without system shutdown.

Primary and redundant blowers are installed on each filter system with automatic changeover controls. Exhaust stacks rise about 10 meters above-ground. Both the blowers and the filters are outside the laboratory.

All laboratory drains connect to a pair of 6,000-gallon underground fiberglass tanks. There the liquid waste is sampled, treated as necessary, and disposed. The tanks are equipped with a remote level indicator with high and low alarm points.

An emergency generator provides backup power to the blowers, security, and system alarms to allow the laboratory to make an orderly shutdown if required.

The HML is surrounded by approximately 1,000 acres of Battelle-owned property. The area is also available for outdoor testing and research programs.

Toxic Substance Laboratory (TSL)

All activities involving the storage or handling of toxic substances at the Columbus site are conducted in the Toxic Substances Laboratory. This facility is separated from adjacent Battelle facilities by concrete block walls. There are three doors to this facility located on the same corridor. Two access doors provide entry into the laboratory. A third door is an emergency exit door with no access. All three doors are metal and the two access doors are locked to prevent unauthorized access.

Four laboratory hoods have been provided with face velocities of 150 ± 30 fpm. An alarm has been incorporated into the ventilation system in case of failure. A glovebox has been provided for use in weighing toxic substances. The exhausts from both the hoods and the glovebox have been equipped with HEPA filtering systems to prevent discharge of toxic agents into the atmosphere. The filter system is checked each time a filter is changed. Three doors providing exits from all areas of the laboratory have been installed.

The HEPA filters on the hood exhausts are changed periodically as required. The hoods are equipped with automatic monitoring devices which indicate reduced air flow due to filter clogging. Protective clothing is worn when the filters are changed and the used filters, assumed to be contaminated with toxic substances, are stored for future decontamination and disposal.

The laboratory has also been equipped with shower facilities and eyewash fountains. In addition, all laboratory benches have been equipped with stainless steel pans to contain spills for each of cleanup and detoxification.

Personnel protective gear is provided including disposal laboratory overalls, safety glasses and goggles, and gloves.

APPENDIX II

SUBTASK 3. CHEMICAL CONCEPTS PRELIMINARY SCREENING

TEST REPORT

for

TASK 3 SUBTASK 3
CHEMICAL CONCEPTS PRELIMINARY SCREENING
CONTRACT DAAK11-81-C-0101

to

UNITED STATES ARMY
TOXIC AND HAZARDOUS MATERIALS AGENCY

by

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EXECUTIVE SUMMARY

A Preliminary evaluation of the five chemical decontamination concepts identified in Phase 1 of the Novel Processing Program was performed. The concepts which were evaluated in laboratory scale glassware included monoethanolamine (neat and 50 percent aqueous solution), aqueous solution of 1-octylpyridinium 4-aldoxime bromide (OPAB), anhydrous ammonia, steam and steam/ammonia.

The results indicate that all of the chemical decontaminants were effective on specific chemical agents. The most promising concepts, involving the use of either steam or OPAB, achieved high destruction efficiencies for all three agents (HD, GB and VX). As such the steam and the OPAB concepts were selected for further evaluation in subsequent subtasks involving decontamination of steel and concrete matrices. Because of the effectiveness of the other chemical decontaminants, no concept will be eliminated at this time. Rather, all remaining concepts will be retained in the event that an alternative decontaminant is required in the subsequent efforts.

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UNITED STATES ARMY
TOXIC AND HAZARDOUS MATERIALS AGENCY

1.0 INTRODUCTION

In the previous phase (Task 1), ideas were systematically developed into concepts for decontaminating buildings and equipment. These concepts were evaluated and ranked with respect to technical and economic factors. Knowledge gaps relating to application of the concepts were selected for laboratory evaluation in Task 3 including five concepts utilizing chemical reactions as the decontamination technique (OPAB, MEA, Steam, NH_3, NH_3/Steam). This report details the results of the preliminary laboratory evaluation of these five chemical decontamination concepts using neat agents.

2.0 OBJECTIVES

The objective of this study was to provide preliminary evaluation of the five proposed chemical decontamination concepts so that the list of promising candidates is narrowed to three or less with the minimum experimental effort. The chemical concepts evaluated were:

- Monoethanolamine (MEA) - neat and 50% aqueous solution
- Aqueous solution containing a surfactant and 1-octyl pyridinium 4-aldoxime bromide (OPAB)
- Anhydrous NH_3
- Steam
- Steam/NH_3

The primary criterion for evaluation was destruction of agent so that the minimum amount of agent remained unaltered following the chemical treatment. Secondarily, rate of agent destruction was considered. Toxicity of by-products was also taken into account by attempts at by-product identification through GC-MS.

3.0 FACILITIES AND EQUIPMENT

Since neat munition grade agents (HD, GB, VX) were used in the tests, the experiments were performed in hoods located at Battelle's Hazardous Materials Laboratory (HML).

Analyses were done by gas chromatography (GC) or gas chromatography coupled with a mass spectrometer (GC-MS). A Varian Model 3700 GC equipped with a Varian Flame Photometric Detector (FPD) was used. This detector has two modes of use, the P mode (phosphorus), and the S mode (sulfur). The P mode was used when analyzing for the phosphorus-containing agents, GB and VX. The S mode was used when analyzing for one of the sulfur-containing agents, HD. The column used in the GC was a 3 percent SP 2100-DBon 100/120 Supelcoport (6 feet long, 0.25 inches O.D., 4 mm I.D.).

The GC-MS used for analysis was a Finnagan Model A 1020 using electron impact as the mode of ionization. The scan range and cycle time was 40-450 amu/second. A fused silica capillary column coated with DB5 (30 meters x 0.025 mm) was used for GC separation.

Each of the five proposed chemical decontaminants has its own characteristics and therefore was treated individually. For the gaseous systems (steam, ammonia, and steam and ammonia combined), the gaseous reactant apparatus illustrated in Figure 1 was designed. The apparatus allowed only vapor, not condensed liquid, to contact the agent.

The reagent (water, anhydrous ammonia, or aqueous ammonia) was contained in a boiling flask. Connected to the neck of the flask was an extension tube into which an inert Teflon® plug was inserted for the purpose

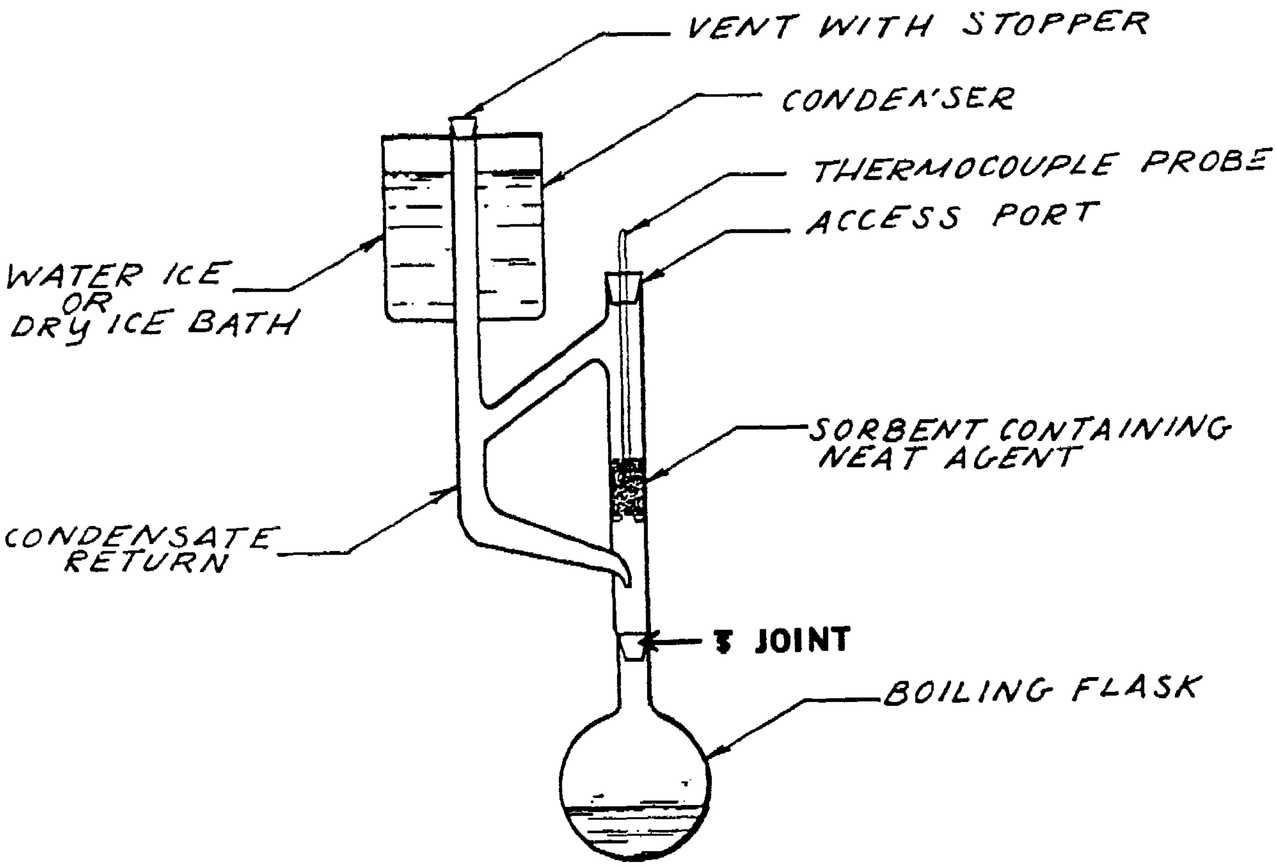

FIGURE 1. GASEOUS REACTANT APPLICATION APPARATUS

of retaining the agent under examination. A reflux condenser, located above the extension tube, served to return decontaminant to the boiling flask. Water ice was used in the condenser when operating with either steam or NH_3/steam, while dry ice (mp = -78.5 C) was used when operating with NH_3. When operating with liquid ammonia (boiling point = -33 C), the sorbent plug was maintained at room temperature.

More flexibility was available for the two liquid systems. Undiluted (neat) agent was placed in a 100 ml beaker containing a magnetic stirrer. Liquid reactant (OPAB solution or MEA) was added and the mixture stirred. Reaction kinetics in terms of residual agent were observed by withdrawing aliquots at specified intervals.

4.0 EXPERIMENTAL PROCEDURES

A USATHAMA approved test plan was used as the basis for conducting the experiments. Actual laboratory and analytical data are given in Battelle Laboratory Record Book No. 39064 and 39108.

For each of the five chemical concepts, a baseline experiment was performed to determine recovery efficiency. For OPAB and 50 percent MEA and neat MEA, this involved spiking the decontaminating solution with each agent, stirring a few seconds, and removing an aliquot for GC analysis. For steam and ammonium hydroxide (NH_3/steam), this involved spiking water or ammonium hydroxide with each agent, stirring a few seconds, and removing an aliquot for GC analysis. A similar experiment was not done for anhydrous ammonia since there was no liquid remaining in the pot to be extracted. Instead, the recovery data from the baseline experiment with VX and the gaseous application apparatus described above were used.

Recovery efficiencies of agent from solution of decontaminant are given in Table 1. The baseline experiments indicated that extraction of either HD or GB from MEA required acidification to pH 3 with acetic acid in order to achieve desirable recovery efficiencies. However, in the case of VX,

TABLE 1. RECOVERY EFFICIENCIES OF AGENT FROM DECONTAMINANTS

Agent	Decontaminant	Amount of Agent Spiked, mg	Amount of Agent Recovered,[a] mg	Recovery Efficiency,[b] %
HD	50% MEA	317	297.5	93.8
GB	50% MEA	287	39.9	13.9
VX	50% NEA	323	219.4[c]	68.5
VX	100% MEA	324	214.3[c]	66.1
HD	5% OPAB	279	371.3[c]	133.1
HD	5% OPAB	279	387.4[c]	138.9
GB	5% OPAB	283	(d)	(d)
VX	5% OPAB	282	88.3[c]	31.3
VX	5% OPAB	282	91.3[c]	32.4
GB	H_2O	10	5.24[c]	52.4
GB	NH_4OH	10	7.80[c]	78.0

a) The decontaminant solution was spiked with agent while stirring. A sample was immediately withdrawn and extracted with hexane or methylene chloride. The extract was then analyzed for agent using a gas chromatograph equipped with a flame photometric detector (GC/FPD).

b) Recovery efficiency (%) = 100 x (Agent recovered (mg) ÷ Agent spiked (mg))

c) Average of two analyses.

d) Interferences prevented the use of the GC/FPD. The samples were analyzed by a GC/mass spectrometer.

extraction from MEA was performed without acidification. The recovery efficiency of VX from a 50 percent solution of MEA using methylene chloride was 109 percent without acidification while only 5.3 percent of the VX spiked was recovered upon acidification.

In addition to the decontaminant extraction experiments, several baseline tests were performed with the gaseous reactant apparatus. A hexane wash of the apparatus containing the Teflon® wool plug (no agent) was performed to determine if interferences were present. Analysis of the hexane by gas chromatography indicated the sample was clean (i.e., no observable peaks). The apparatus was reassembled and 10 mg of neat VX was applied to the Teflon® wool plug. The apparatus, including the plug, was then extracted with 30 ml of hexane. Analysis of the hexane indicated that 10.8 mg of VX was extracted (108 percent recovery efficiency). A second extraction of the apparatus with 30 ml of hexane indicated that 0.042 mg (0.42 percent of original spike) was extracted. The Teflon® wool was then removed from the apparatus and separately extracted. No agent was detectable in this extract.

Munition grade agents used in these experiments were compared to SARMs (PA796, PA1126, and PA1128) by GC to determine if adjustments were needed in amounts of agent delivered to the reaction vessels. Munition grade rather than high purity agent was selected for use in these studies because buildings used to manufacture and handle agent will most likely be contaminated with munition grade rather than high purity agent. Also, munition grade agent may be considered as being the worst case since it may contain stabilizers which either inhibit decomposition reactions or lead to agent reformation. Agents were delivered with Eppendorf pipettes; and the density of each was taken into account in calculations.

Table 2 outlines the experimental procedures and analysis conditions for the evaluation of the chemical decontamination concepts. Sections 4.1 to 4.6 describe these procedures in more detail. All experiments were run in duplicate and each experiment had two aliquots withdrawn at each interval for GC analysis.

GC-FPD analyses were all performed on the same column (SP2100 - see Section 3.0) using different temperature programs. For all HD analyses, the program was 135 C isothermal. For all VX analyses, the program

TABLE 2. SUMMARY OF EXPERIMENTAL PROCEDURES

Decontamination Concepts	GB	HD	VX
50% MEA	Acidify with acetic acid[e] Extract with CH_2Cl_2 Analyze by GC-MS[d]	Acidify with acetic acid[e] Extract with CH_2Cl_2 Analyze by GC-FPD[b]	Extract with CH_2CL_2 Analyze by GC-FPD[a]
100% MEA	Acidify with acetic acid[e] Extract with CH_2Cl_2 Analyze by GC-MS[d]	Acidify with acetic acid[e] Extract with CH_2Cl_2 Analyze by GC-FPD[b]	Extract with CH_2Cl_2 Analyze by GC-FPD[c]
Steam	Extract pot with CH_2Cl_2 Extract apparatus with hexane Extract wool with CH_2Cl_2 Analyze by GC-FPD[a]	Extract pot with CH_2Cl_2 Extract apparatus with hexane Extract wool with CH_2Cl_2 Analyze by GC-FPD[b]	Extract pot with CH_2Cl_2 Extract apparatus with hexare Extract wool with CH_2Cl_2 Analyze by GC-FPD[c]
Anhy. Ammonia	Same as steam	Same as steam	Same as steam
Ammonium Hydroxide	Same as steam[f]	Same as steam	Same as steam
OPAB	Extract with CH_2Cl_2 Analyze by GC-MS[d]	Extract with CH_2Cl_2 Analyze by GC-FPD[b]	Extract with CH_2Cl_2 Analyze by GC-FPD[c]

(a) Column: SP 2100; Program: 100 C (hold 1 minute) to 240 C at 90 C/minute; FPD detector; in P mode

(b) Column: SP 2100; Program: 135 C isothermal; FPD detector: in S mode

(c) Column: SP 2100; Program; 190 C (hold 4 minutes) to 240 C at 35 C/minute (hold 4 minutes); Detector in P mode

(d) Column: DB 5; Program: 35 C (1 minute hold) to 250 C at 12 C/minute (hold 2 minutes); Mass spectrometer: splitless, EI, range 40-450 amu/sec.

(e) To pH 3 using dilute acetic acid

(f) GC/MS analysis required because of analytical interferences with the GC-FPD approach

was 190 C (with 4-minute hold) to 240 C at 35 C/minute (with 4-minute hold). For all GB analyses run on GC-FPD, the program was 100 C (with 1-minute hold) to 240 C at 90 C/minute. For all GB analyses run on GC-MS, the program (on a DB5 column) was 35 C (with 1-minute hold) to 250 C at 12 C/minute (with 2-minute hold).

The detection limit of the standard curve for each of the agents (GB, VX, and HD) was 2 μg/ml. Quantification of the peaks was possible at a concentration of 5 μg/ml. These detection limits apply to agent in the final solution being analyzed.

4.1 Experiments with 50 Percent Monoethanolamine (MEA)

4.1.1 50 Percent MEA/VX

Eighty ml of a 50 percent solution of monoethanolamine and distilled water (by weight) were placed in a 150-ml beaker and stirred at room temperature for five minutes. VX, in the amount of 322.7 mg, was then added and stirring continued. At intervals of 10, 20, 40, 60, 120, 240, 1440 minutes, 5-ml aliquots of the mixture were removed and extracted once with 5 ml of methylene chloride. The extract was then analyzed by GC-FPD for VX.

4.1.2 50 Percent MEA/GB

These experiments were performed as above with VX except that 287.0 mg of GB were spiked into the beaker and each 5-ml aliquot removed was brought to pH 3 by addition of 40 ml of 63 percent acetic acid prior to extraction with methylene chloride. GC analyses showed no change in the amount of GB present over time. Since literature reports noted fast reaction of MEA and GB, the experiment was repeated using GC-MS as the detector for GB. The second experiment was similar to the first except for the intervals at which aliquots were drawn, 1 and 20 minutes. GC-MS analyses showed that GB was reacting with MEA to form a decomposition product that had an identical retention time on GC as GB, thus no change in the GB peak on GC was observed in the first experiment.

4.1.3 50 Percent MEA/HD

These experiments were performed in a manner similar to 50 percent MEA and VX. HD, in the amount of 317.0 mg, was spiked. The intervals for removing aliquots were the same except no 1440-minute aliquot was taken. Again, each aliquot removed was brought to pH 3 by addition of 40 ml of 63 percent acetic acid prior to extraction and analysis by GC-FPD.

The reaction mixture in the beaker in this case, however, was not always a single phase. Yellow beads of HD were initially observed, but as the reaction approached completion, the reaction mixture became homogeneous, indicating the decontamination product(s) are more soluble in 50 percent MEA than HD.

4.2 Steam

4.2.1 Steam/HD

This experiment was performed using the gaseous-reactant application apparatus described in Section 3.0. HD, in the amount of 101.5 mg, was spiked on the Teflon wool plug. Distilled water, in the amount of 50 ml, was placed in a 100-ml round bottom flask and refluxed for 5, 20, or 60 minutes. The apparatus was allowed to cool after each reflux period, the flask was removed, and a 5 ml aliquot from the flask was extracted with 5 ml of methylene chloride. Hexane, in the amount of 30 ml, was then placed in a new 100-ml round bottom flask and placed under the apparatus. The condenser was moved to the access port (see Figure 1), and the hexane left to reflux for one hour. The Teflon plug was then removed and extracted in 5 ml of methylene chloride. The extracts from the condensate, the hexane rinse, and the plug rinse were all analyzed by GC-FPD.

4.2.2 Steam/GB

This experiment was performed in a manner similar to Steam/HD except 97.9 mg of GB were spiked onto the Teflon wool. The boiling water

was refluxed for periods of 20, 60, or 120 minutes. Each of the three extracts were analyzed by GC-FPD.

4.2.3 Steam/VX

This experiment was performed in a manner similar to Steam/GB except 100.9 mg of VX were spiked onto the Teflon wool. Each of the three extracts were analyzed by GC-FPD.

4.3 Experiments with Anhydrous Ammonia

4.3.1 Anhydrous Ammonia/GB

This experiment was performed in a manner similar to the Steam GB experiment except a dry ice condenser was used in place of the water condenser. GB, in the amount of 59.9 mg, was spiked on the Teflon wool plug. After refluxing for 20, 60 or 120 minutes, the dry ice condenser was removed and the ammonia evaporated. The 100-ml round bottom flask contained some water condensed from the air, but no ammonia. The flask was extracted with methylene chloride as in the steam experiments. The three extracts were analyzed by GC-FPD.

4.3.2 Anhydrous Ammonia/HD

This experiment was performed in a manner similar to the Anhydrous Ammonia/GB experiment, except 63.4 mg of HD were spiked on the Teflon wool plug. Only a 60-minute reflux experiment was performed. Each of the three extracts from this experiment were analyzed by GC-FPD.

4.3.3 Anhydrous Ammonia/VX

This experiment was performed in a manner similar to the Anhydrous Ammonia/GB experiment except 60.5 mg of VX were spiked on the Teflon wool. Each of the three extracts were analyzed by GC-FPD.

4.4 Experiments with Ammonium Hydroxide (NH_3/Steam)

4.4.1 Ammonium Hydroxide/GB

This experiment was performed in a manner similar to Steam/GB except 98.0 mg of GB were spiked on the Teflon wool plug and only a single 60-minute reflux experiment was performed. Each of the three extracts were analyzed by GC-FPD.

4.4.2 Ammonium Hydroxide/HD

This experiment was performed in a manner similar to Ammonium Hydroxide/GB except 101.5 mg of HD were spiked on the Teflon wool. Each of the three extracts were analyzed by GC-FPD.

4.4.3 Ammonium Hydroxide/VX

This experiment was performed in a manner similar to Ammonium Hydroxide/GB except 55.5 mg of VX were spike on the Teflon wool plug. Each of the three extracts were analyzed by GC-FPD.

4.5 Experiments with OPAB

Two OPAB formulations were evaluated. The BF-OPAB formulation furnished by Battelle-Frankfurt, was composed of 5 weight percent 1-octylpyridimium 4-aldoxime bromide sodium salt, 1 percent foam stabilizers, 5 percent polyethyleneglycol and 89 percent water. The BCL-OPAB formulation, synthesized in-house*, was composed of 5 weight percent 1-octylpyridinium 4-aldoxime bromide and 95 percent water. The experimental procedures, which were identical for each OPAB formulation, are described as follows.

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* Synthesized under ARO-STAS TCN-84-273.

4.5.1 OPAB/GB

GB, in the amount of 283.1 mg, was spiked into 140 ml of OPAB in a 150-ml beaker. While the solution was being stirred at room temperature, 10-ml aliquots were removed at intervals of 0, 20, and 40 minutes. The aliquots were extracted once with 10 ml of methylene chloride. These extracts were analyzed by GC-MS and GC-FPD.

4.5.2 OPAB/HD

This experiment was performed in a manner similar to OPAB/GB except 279.0 mg of HD were spiked into the OPAB solution. The aliquots were removed at 20, 40, 60, 180, 240, and 360 minutes. The methylene chloride extracts of these aliquots were analyzed by GC-FPD.

4.5.3 OPAB/VX

This experiment was performed in a manner similar to OPAB/GB except 283.0 mg VX were spiked into the OPAB solution. The aliquots were removed at 20, 40, 60, 180, 240, 360, and 1440 minutes. The methylene chloride extracts were analyzed by GC-FPD.

4.6 Experiments with 100 Percent MEA

4.6.1 MEA/GB

This experiment was performed in a manner similar to 50 percent MEA/GB. The 5-ml aliquots were removed from the spiked mixture at intervals of 0 and 20 minutes. Acidification of these aliquots was accomplished with 40 ml of 63 percent acetic acid. The aliquots were extracted with 5 ml methylene chloride and the extracts were analyzed by GC-MS.

4.6.2 MEA/HD

This experiment was performed in a manner similar to MEA/GB except 317 mg of HD were spiked into the MEA. The 5-ml aliquots were removed at

intervals of 1, 30, and 60 minutes. After acidification as in the case of MEA/GB, the aliquots were extracted with 5 ml methylene chloride and the extracts were analyzed by GC-FPD.

This experiment was performed in a manner similar to MEA/GB except 317 mg of HD were spiked into the MEA. The 5-ml aliquots were removed at intervals of 1, 30, and 60 minutes. After acidification as in the case of MEA/GB, the aliquots were extracted with 5 ml methylene chloride and the extracts were analyzed by GC-FPD.

4.6.3 MEA/VX

This experiment was performed in a manner similar to the other MEA experiments except 322.7 mg of VX were spiked into the MEA. The CH_2Cl_2 extracts were analyzed by GC-FPD.

5.0 ANALYTICAL RESULTS

Tables 3 and 4 summarize the analytical results of the text experiments. (See Appendix A for the detailed results of all experiments.)* Table 3 lists the time in each reaction that no detectable agent is present if that point occurred. If not, the highest destruction efficiency observed is described. "Time" indicates reaction time, "Resid" indicates milligram amount of agent still present, and "% D" indicates percentage destruction efficiency, which was calculated by the following equation:

$$\% \text{ Decon Effectiveness} = \left[\frac{[\text{agent}]_{\text{initial}} - [\text{agent}]_{\text{time } x}}{[\text{agent}]_{\text{initial}}}\right] \times 100$$

It can be seen from Table 3 that the decontaminants selected in Task 1 are effective decontaminants for each agent and that, as anticipated, VX is the most resistant to destruction. Displaying an unexpected efficiency in destroying HD as well the expected GB and VX destruction,

* Sample chromatograms are given in Appendix B and sample mass spectra and given in Appendix C.

TABLE 3. SUMMARY OF ANALYTICAL RESULTS

Decontam-ination Concepts	GB Time (min)	GB Resid (mg)	GB % D	HD Time (min)	HD Resid (mg)	HD % D	VX Time (min)	VX Resid (mg)	VX % D
50% MEA	1	BDL[a]	99.8	240	BDL	99.9	1440	52.8	83.6
Steam	120	BDL	99.8	20	BDL	99.8	120	0.5	99.5
Anhydrous Ammonia	60	0.8	98.6	60	57.3	9.7	60	8.6	85.8
NH_3/Steam	60	BDL	(c)	60	BDL	99.8	60	19.5[b]	80.7[b]
BF-OPAB	1	BDL	99.8	360	BDL	99.8	240	BDL	99.8
100% MEA	1	BDL	99.8	240	BDL	99.9	1440	173.0	46.0

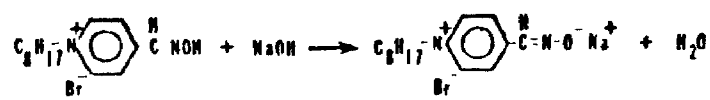
(a) BDL = Below Detection Limit (<2 μg/ml)
(b) Average of duplicate experiments: Resid = 31.0 and 7.9; % D = 69.3 and 92.1, respectively.
(c) Analyzed by GC/MS

TABLE 4. SUMMARY OF RESULTS FROM OPAB BEAKER TESTS

Agent	Sample Time(c), min.	BCL-OPAB[a] Residual Agent, mg	BCL-OPAB[a] Decon. Efficiency,[d] percent	BF-OPAB[b] Residual Agent, mg	BF-OPAB[b] Decon. Efficiency,[d] percent
GB	1	35.8	87.3 [f]	<0.2[e]	>99.9
GB	20	33.5	88.2 [f]	--	--
HD	40	<0.21	>99.9	105.8	62.1
HD	360	<0.21	>99.9	<0.1	>99.9
VX	20	0.53	99.8	41.9	85.2
VX	240	0.31	99.9	<0.2	>99.9

(a) BCL-OPAB = 5 weight percent OPAB (synthesized at Battelle-Columbus) dissolved in water.

(b) BF-OPAB = 5 weight percent OPAB as the sodium salt, 1 weight percent foam stabilizer and 5 weight percent polyethyleneglycol (anti-freezing agent) dissolved in water. Note: the sodium salt of OPAB is prepared by the following reaction:



(c) Sample time = Time after OPAB solution was spiked with agent.

(d) Decon. efficiency = 100 x [1 - Residual agent (mg)/Agent spiked (mg)].

(e) Analyzed by GC/MS because of agent interferences.

(f) The apparently low decon efficiency was probably caused by decomposition product(s) which interfered with GC/FPD analysis.

OPAB appears to be the single reagent of greatest promise. Steam is also seen to show excellent results in decontaminating all three agents.

A comparison of the results from the OPAB beaker experiments utilizing the two different OPAB formulations are shown in Table 4. The results suggest that the BCL-OPAB formulation (neat OPAB dissolved in water) was more effective in destroying HD and VX and less effective in destroying GB than the BF-OPAB formulation (sodium salt of OPAB and additives dissolved in water). It is important to note that the residual GB detected in the experiments using the BCL-OPAB formulation may be a decomposition product(s) which interferes with the GC/FPD analyses for GB. Previous work in Subtask 3 involving the BF-OPAB formulation required the use of GC/MS to quantitatively analyze for GB because of interferences which resulted when GC/FPD was used.

The activity of OPAB for destruction of HD appears to be related to the solution formulation. The BCL-OPAB formulation (neat OPAB dissolved in water) is slightly acidic (pH 4 to 5) whereas the BF-OPAB formulation (sodium salt of OPAB and additives dissolved in water) is basic (pH 9 to 10). The slightly acidic OPAB formulation appears to be more reactive with HD than the basic OPAB formulation. However, the basic OPAB formulation may still be preferred for nerve agent decontamination.

Although not specifically investigated, information on the degree of agent reformation in reaction solution was obtained from the kinetic data. In most experiments where kinetic data was obtained, the destruction of agent increased with time thereby indicating that agent reformation did not occur. One exception is for anhydrous ammonia and VX. Results (see Appendix A) indicate a lower destruction for the 120 minute experiments than for the 60 minute experiments. The lower destruction may be due to either reformation of VX or ice formation on the neck of the reaction vessel which occurred during the 120-minute experiments but not the 60 minute experiments (the ice may have lowered the reaction temperature at the Teflon plug).

Mass spectral data was obtained on several selected reactions, namely Steam/HD, GB, VX; OPAB/HD, GB, VX; 50% MEA/GB; 100% MEA; NH_3-Steam/GB, VX and VX/NH_3. Table 5 summarizes the interpretation of the mass spectral data. The table includes comments pertaining to the confidence of the

TABLE 5. MASS SPECTRAL DATA OF AGENT DEGRADATION PRODUCTS

Decontamination Reaction	Compound	Comments	Source: Chemical Decontamination	Source: Impurity
VX/NH_3; 60 minutes; hexane rinse	$CH_3P(=O)(OCH_2CH_3)OCH_2CH_3$	P-S bond broken; OCH_2CH_3 ligand may come from cleavage of a phosphate polymer by displaced OCH_2CH_3 as below. $CH_3P(=O)(OCH_2CH_3)OCH_2CH_3\text{-}O\text{-}P(=O)(CH_3)\text{-}O\text{-}P(=O)(CH_3)\text{-}$	x	
	$CH_3P(=O)(X)OCH_2CH_3$	P-S bond broken; unknown donor X=?	x	
	$HS\text{-}CH_2CH_2N\text{-}(CH(CH_3)_2)_2$	P-S bond broken; thiol left; dotted line indicates probable identification of fragment	x	
VX/NH_3; 60 minutes; Teflon plug extract	trichloromethane	Good fit; stabilizer		x
	cyclohexane	Solvent artifact or from stabilizer ($C_6H_{11}N{=}C{=}NC_6H_{11}$)		x
VX/NH_3; 60 minutes; pot extract	$X\text{-}SCH_2CH_2N\text{-}CH(CH_3)\text{-}CH(CH_3)\text{-}CH(CH_3)CH_3$	P-S bond broken; then sulfur react with X; X=? unknown donor, possibly oxidation of thiol to $-S(=O)-OH$.	x	
	Trichloromethane	Good fit; stabilizer		x
VX/Steam;	$CH_3P(=O)(OCH_2CH_3)OCH_2CH_3$	P-S bond broken; OCH_2CH_3 ligand may be from cleavage of phosphate polymer as shown for VX/NH_3	x	
	cyclohexane	Stabilizer or solvent artifact		x

TABLE 5. (Continued)

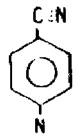
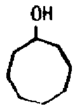
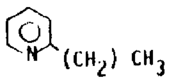
Decontamination Reaction	Compound	Comments	Source: Chemical Decontamination	Source: Impurity
GB/OPAB		OPAB fragment or impurity		x
	1-(2-Propenyloxy)-2-propanol	Good fit; unknown origin; possibly solvent artifact		x
		Possibly solvent artifact		x
	$CH_3\overset{O}{\overset{\Vert}{P}}\text{-O-}\overset{CH_3}{\overset{\vert}{C}H}CH_3$; $\overset{\vert}{O}\overset{}{C}HCH_3$; $\overset{\vert}{C}H_3$	P-F bond broken; similar to VX/NH_3, the ligand $\overset{\vert}{O}\underset{CH_3}{\underset{\vert}{C}H}CH_3$ attacks after being displaced by formation of phosphate polymer	x	
	$C_8H_{17}Br$	Good fit; OPAB fragment or impurity		x
	$H\text{-}\overset{O}{\overset{\Vert}{C}}NH\text{-}C_8H_{17}$	Weak spectrum; OPAB fragment or impurity		x
		Possibly an OPAB fragment or impurity		x
GB/50% MEA	$CH_3CH_2\overset{O}{\overset{\Vert}{C}}O\overset{CH_3}{\overset{\vert}{C}H}CH_3$	Good fit; solvent impurity or stabilizer		x
	$CH_3CH_2CH_2\overset{O}{\overset{\Vert}{C}}OCH_2CH_3$	Good fit; solvent impurity or stabilizer		x

TABLE 5. (Continued)

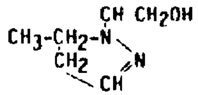
Decontamination Reaction	Compound	Comments	Source: Chemical Decontamination	Source: Impurity
	$CH_3COCH_2CH_2CH_2CH_3$	Good fit; solvent impurity or stabilizer reaction		
	$CH_3CH_2CH_2C(O)OCH(CH_3)CH_3$	Good fit; solvent impurity or stabilizer reaction		x
		Good fit, solvent impurity or stabilizer reaction		x
(also at 15 seconds)	$CH_3P(O)(OCH(CH_3)CH_3)-O-CH(CH_3)CH_3$	Good fit; P-F bond broken; same as found in OPAB/GB fragment	x	
(also at 15 seconds)	$CH_3C(O)OCH_2CH_2OC(O)CH_3$	Good fit; solvent impurity or stabilizer reaction		x
		Good fit; solvent impurity		x
	$CH_3P(O)(OH)-O-CH(CH_3)CH_3$	Probable fragment; P-F bond broken	x	
VX/100% MEA	$X-SCH_2CH_2N(CH(CH_3)_2)_2$	P-S bond broken; good fit	x	

TABLE 5. (Continued)

Decontamination Reaction	Compound	Comments	Source: Chemical Decontamination	Source: Impurity
GB/Steam	Butanoic acid, 1-methyl ethyl ester	Solvent impurity		x
	Acetic acid, butyl ester	Solvent impurity		x
	Ethylene glycol diacetate	Solvent impurity		x
	$CH_3P(=O)(OCH(CH_3)_2)OCH(CH_3)_2$	P-F bond broken	x	
	1-Butanamine, N, N-Dibutyl	Stabilizer?		x
GB/NH_3 - Steam	$CH_3P(=O)(OCH(CH_3)_2)OCH(CH_3)_2$	P-F bond broken	x	
	CH_2Cl_2	Solvent impurity		x
HD/OPAB	$\overline{SCH_2CH_2SCH_2CH_2}$	C-Cl bond broken	x	
	Dibromo - ?	OPAB impurity or fragment		x

TABLE 5. (Continued)

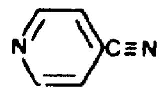
Decontamination Reaction	Compound	Comments	Source: Chemical Decontamination	Source: Impurity
HD/Steam	$\overline{SCH_2CH_2SCH_2CH_2}$	C-Cl bond broken	x	
	Toluene	Solvent impurity		x
	$CH_3CH_2\overset{O}{\overset{\Vert}{S}}CH{=}CH_2$	C-Cl bond broken, sulfur oxidized	x	
	Ethylene glycol diacetate	Solvent impurity		x
VX/NH_3 - Steam	$((CH_3)_2CH)_2N(CH_2)_2NH_2$	Stabilizer?		x
	$((CH_3)_2CH)_2N(CH_2)_2OH$	Stabilizer?		x
	$CH_3\overset{O}{\overset{\Vert}{P}}(OCH_2CH_3)SCH_2CH_3$	C-N bond broken	x	
	$H_2N\overset{S}{\overset{\Vert}{C}}N(CH(CH_3)_2)_2$	P-S bond broken	x	
	VX	--		
	N, N-bis-isopropylbutane amine	Stabilizer?		x
	Butyl isopropylamine	Stabilizer?		x
	N-alkyl urea	Stabilizer?		x
VX/OPAB		OPAB reaction product	x	
	Octanol	OPAB impurity or fragment		x

TABLE 5. (Continued)

Decontamination Reaction	Compound	Comments	Source	
			Chemical Decontamination	Impurity
VX/OPAB, Cont.	1- Bromooctane	OPAB impurity or fragment		x
	$CH_3P(=O)(SCH_2CH_3)(OCH_2CH_3)$	C-N bond broken	x	
	Octylpyridine	OPAB impurity or fragment		x
	Octane, 1,1' - oxybis-	OPAB impurity or fragment		x
	Octylpyridyl ketone	OPAB impurity or fragment		x

identification indicated, as well as the implication of the presence of the compound identified. Where possible the table also lists the source of an identified compound. The compounds derive from either chemical reaction of the decontaminant, agent with the reaction of impurities such as solvents and stabilizers added to the agents prior to use, or the presence of other impurities. The stabilizers include diisopropylcarbodiimide and dicyclohexylcarbodiimide found in all the agents and dibutylamine found in GB only.

In addition to product identification attempts, GC/MS data was generated to confirm decontamination on selected experiments. For example, the mass spectra for the NH_3-steam decontamination of GB and VX were obtained to verify that the apparently low decontamination effectiveness observed in initial tests was caused by interferences. GC/MS results from the GB/NH_3-steam experiments indicate that the compound with the largest peak area in the chromatogram of the extract (see Appendix B) is diisopropylmethylphosphonate, a transesterification product of GB hydrolysis. GB was not detected by GC/MS in the extract. With an estimated detection limit of 25 μg GB/ml x 30 ml = 0.75 μg GB, approximately 98 percent of the GB was destroyed by the NH_3-steam treatment in 60 minutes. This is comparable to the destruction efficiency achieved using either anhydrous ammonia alone or steam alone. Therefore, the initially reported low GB destruction efficiency by NH_3-steam was due to an interference in the GC/FPD analysis method. GC/MS analysis of the VX/NH_3-steam extract did, however, indicate residual VX remained following 60 minutes of the NH_3-steam treatment (See Figure C17 in Appendix C). Although the VX peak size was not quantified, it is likely that sufficient VX was present to account for the relatively low destruction efficiency previously observed (i.e., 80.7 percent of VX was decontaminated after being in contact with NH_3-steam for 60 minutes).

6.0 COMPARISON OF RESULTS WITH SOME LITERATURE REPORTS

It is interesting to observe the correlation (or contrast) between results obtained in this subtask and some of those reported in the literature.

Rossmann[1] reports a halflife of 8.6 minutes at 20 C for VX in OPAB (OPAB, foam stabilizer, polyethylene glycol and water) and 1.8 minutes for DFP (diisopropyl fluorophosphonate) under the same conditions. The results from the current experiments indicate destruction of VX to be below the detection limit (99.8 percent destruction) between 60 and 180 minutes (intermediate intervals were not explored) which is in good agreement with the 78 minutes (9 halflives) required by Rossmann's value for 99.8 percent destruction. There appears to be no literature data for the destruction of GB and HD by OPAB.

Monoethanolamine (MEA) is reported to destroy HD. At 25 C HD was observed[2] to have a halflife of 321 minutes in neat MEA. More rapid results were observed in the current experiments where 50 percent aqueous MEA achieved 99.9 percent destruction of HD in 240 minutes. It has been rationalized[3] that GB and MEA (aqueous or anhydrous) should react rapidly and this was observed to be the case (see Appendix A). Additional information is available concerning MEA in combination with other components (e.g. solvents, caustic) but direct comparison with the current results is not applicable.

Attempts to decontaminate HD contaminated clothing with 10 percent anhydrous NH_3 were reported to be unsuccessful[4]. This confirms the low decontamination efficiency of 9.7 percent obtained from our experiments. No unclassified reports were located which report tests on the decontamination efficiency of GB or VX with anhydrous NH_3.

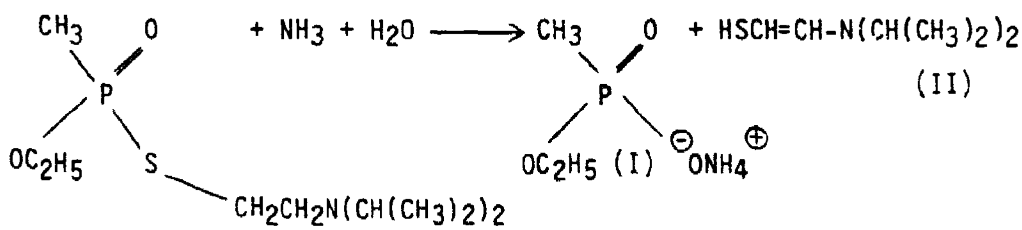
While good results were observed with aqueous ammonia in the vapor phase (i.e. NH_3/steam) against HD, results with the VX were less favorable. It has been reported that ammonium hydroxide at 100 C hydrolyzes VX rather slowly[5] and this appears to confirm the current observations.

Steam alone has been reported to decontaminate HD to very low residue (99.95 percent removal) levels in as little as 10 minutes if the contaminated surface, in this case painted steel, is not preheated.[6] Current experimental results indicate the disappearance of 99.8 percent HD in 20 minutes under somewhat different conditions.

In general, then, where the literature contains data obtained under conditions close enough to those employed in this subtask to permit at least rough comparisons to be made, there are no major discrepancies between this work and that of others.

In terms of the results obtained by MS analysis of selected reactions, some correspondence with literature was found. Rossmann(1) predicted that the reaction between OPAB and GB would be a nucleophilic displacement of the fluorine to produce HF and the phosphoric acid of GB. While the phosphoric acid was not directly observed, the P-F bond was broken. It has been reported[7] that phosphorus-containing agents form polymers called "pyro" agents upon reaction at the phosphorus-fluorine or phosphorus-sulfur bond. MS data reveal a product which could result from hydrolysis of this polymer followed by attack by the displaced ligand, $^{-}OCHCH_3$. Reaction of steam with VX show a reaction similar to the OPAB/GB reaction except that the attacking ligand is $^{-}OCH(CH_3)_2$.

Domjan[4] shows the mechanism for the reaction of $VX+NH_3$ as follows.



The thiol (II) was observed in the reaction product analysis by MS, but not the ammonium phosphinate (I). It is unlikely that such a phosphinate would form a polymer, hydrolyze, and be attacked by a displaced ligand, as discussed above for OPAB/GB and Steam/VX. However, "pyro-VX" was observed by MS, indicating that perhaps the phosphinate does not form or that the "pyro-VX" observed by MS was generated by a different mechanism.

The reaction of MEA and GB in chloroform with triethylamine as proton acceptor is thought[3] to occur as follows:

$$CH_3-\underset{\underset{OCH(CH_3)_2}{|}}{\overset{\overset{O}{\|}}{P}}-F + HOCH_2CH_2NH_2 \longrightarrow CH_3-\underset{\underset{OCH(CH_3)_2}{|}}{\overset{\overset{O}{\|}}{P}}-OCH_2CH_2NH_2 + HF$$

$$HF + Et_3N \rightleftharpoons Et_3N \cdot HF$$

The author warns, however, that these results may not be used to forecast the reactivity of aqueous MEA with GB, since MEA and water have high dielectric constants which would favor reaction between these materials as opposed to the poor, low dielectric of chloroform. On the basis of the MS results from this study it is difficult to determine whether the phosphate moiety has reacted to form a phosphate amide alcohol or a phosphate ester amine or something else.

7.0 EVALUATION AND RECOMMENDATION

The results of this subtask indicate that all of the decontaminants investigated (50% MEA, Steam, NH_3, NH_3/Steam, OPAB and 100% MEA) were effective to some extent. As such, no concept will be eliminated although a selection of the most promising concepts will still be performed. The less promising concepts will be retained for consideration in the event that an alternative concept(s) is required in subsequent efforts.

Although it is not a requirement of this program that a decontamination system be developed which is applicable to all three agents under consideration, there is a certain logistical advantage to identifying such a universal reagent. With this in mind, the candidate reagents can be summarized as follows.

- MEA - Although MEA (50 percent aqueous and undiluted) is rapidly effective against GB and reacts slowly yet completely (i.e. below detection limit) with HD, it is less effective in decontaminating VX. As such, the performance of MEA is less promising as compared with other systems evaluated.

- NH_3 - Anhydrous ammonia was evaluated in spite of its potential hazards (relatively toxic, gas with explosion limits) because of the advantages arising from the ability of a gaseous reagent to distribute itself throughout a structure and to penetrate inaccessible spaces and surfaces. It was found to have less effective decontaminating properties especially for HD as compared with other decontaminants.

- NH_3/Steam - A mixture of ammonia and steam, i.e. boiling aqueous ammonia, produced somewhat ambiguous results. Because there is no direct evidence that this system is superior to steam alone, the NH_3/steam concept merits no further study at this time.

- Steam - Steam has many obvious advantages for use as a decontaminant. It is inexpensive, non-toxic and easily applied to complex configurations. The principal hazard expected to be associated with its use is the possible risks for burns to operating personnel. Steam is an effective decontaminant: nerve agents are reduced to 1 percent or less residue within two hours and mustard is decomposed in even less time. In field application longer exposure times can be achieved if required. The degradation products of Steam/VX seem innocuous. Steam is an obvious candidate for more extensive evaluation.

- OPAB - The OPAB formulation was specifically developed for and evaluated against VX. The very effective results reported by the Battelle-Frankfurt research group were confirmed in this subtask. In addition, OPAB was demonstrated to be effective against GB as anticipated and against HD which was not expected.

OPAB is a safe material to apply since it is not toxic and can be applied at ambient temperature. OPAB is a relatively low viscosity liquid and the presence of a surface active chemical should enhance spreading. The surface active chemical may be removed to enhance penetration of concrete, if necessary. The degradation products of OPAB/GB seem innocuous. The OPAB system is one of the most effective decontaminants for all three agents examined. One apparent negative attribute of OPAB is the cost, although commercial production of OPAB might reduce its cost significantly.

We recommend that further evaluations be made of the steam and OPAB decontamination methods.

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7. Cox, J. R., Jr. and Ramsay, O. B., <u>Chem Rev, 64,</u> (1964), 317.

APPENDIX A

DETAILED ANALYTICAL RESULTS

TABLE A-1. DETAILED ANALYTICAL RESULTS

Decontamination Concepts	GB Time (min)	GB Resid (mg)	GB % D	HD Time (min)	HD Resid (mg)	HD % D	VX Time (min)	VX Resid (mg)	VX % D
50% MEA	1	BDL[(a)]	99.8	1	213.2	32.7	10	186.4	42.2
	20	BDL	99.8	1	218.8	31.0	10	198.4	38.5
				3	1149.5	>0	20	187.2	42.0
				3	1264.1	>0	20	194.4	39.8
				20	618.0	0	40	189.6	41.3
				20	352.0	0	40	199.2	38.3
				40	183.8	42.0	60	180.8	44.0
				40	257.4	18.8	60	193.6	40.0
				60	133.4	57.9	120	201.6	37.5
				60	no data	--	120	205.6	36.3
				60	741.0	>0	240	182.4	43.5
				60	1.6	99.5	240	262.3	18.7
				120	1.9	99.4	1440	29.6	90.8
				120	107.0	66.2	1440	52.8	83.6
				120	2.4	99.2			
				120	99.7	68.6			
				240	BDL	99.9			
				240	BDL	99.9			
				360	BDL	99.9			
				360	BDL	99.9			
Steam	20	12.8	87.0	5	12.0	88.2	20	5.2	94.8
	20	1.3	(98.7)	5	15.6	84.6	20	5.0	95.0
	60	1213.2μg	(98.3)	20	1.5	98.5	60	3.4	96.6
	60	762.3μg	(99.2)	20	0.9	99.1	60	2.8	97.2
	120	BDL	97.0	20	BDL	99.8	120	0.7	99.4
	120	BDL	97.0	20	BDL	99.8	120	0.5	99.5
				60	BDL	99.8			
				60	BDL	99.8			
				60	0.2	99.8			
				60	BDL	99.8			

TABLE A-1. (Continued)

Decontamination Concepts	GB			HD			VX		
	Time (min)	Resid (mg)	% D	Time (min)	Resid (mg)	% D	Time (min)	Resid (mg)	% D
Anhyd. Ammonia	20	4.6	92.3	60	59.8	5.7	20	4.7	22.0
	20	3.5	94.1	60	57.3	9.7	20	69.0	0
	60	1642.0μg	97.3				60	8.6	85.8
	60	847.0μg	98.6				60	9.4	84.4
	120	2.4	96.0				120	37.1	38.6
	120	2.9	95.2				120	46.9	22.4
NH_3/Steam	60	44.8	54.3 (b)	60	BDL	99.8	60	31.0	69.3 (b)
	60	44.8	54.3 (b)	60	BDL	99.8	60	7.9	92.1 (b)
BF-OPAB	1	BDL	99.8	20	293.4	>0	20	40.6	85.6
				20	291.0	>0	20	43.1	84.7
				40	90.7	67.5	40	19.8	93.0
				40	120.9	56.7	40	23.4	91.7
				60	23.5	91.6	60	10.8	96.2
				60	52.3	81.3	60	12.8	95.5
				180	3.7	98.7	180	0.2	99.8
				180	5.3	98.1	180	BDL	99.8
				240	0.1	99.8	240	BDL	99.8
				240	0.2	99.8	240	BDL	99.8
				360	BDL	99.8	360	BDL	99.8
				360	BDL	99.8	360	BDL	99.8
							1440	BDL	99.8
							1440	BDL	99.8
100% MEA	1	BDL	99.8				1	201.0	38.0
	1	BDL	99.8				1	227.0	30.0
	20	BDL	99.8				20	172.0	46.6
	20	BDL	99.8				20	177.0	45.0

(a) BDL = Below Detection Limit

(b) As determined by GC/FPD, the experiments were subsequently repeated and the samples were analyzed by GC/MS. No residual GB was detected in the repeat experiment. However, intact VX was detected by GC/MS.

APPENDIX B

GAS CHROMATOGRAMS

APPENDIX B

GAS CHROMATOGRAMS

The following sample chromatograms of extracts (i.e. CH_2Cl_2, hexane) obtained after decontamination are given in Appendix B.

Agent	Decontaminant	Figure No.
HD	Steam	B1
HD	OPAB	B2
GB	Steam	B3
GB	NH_3/Steam	B4
VX	NH_3/Steam	B5
VX	100 percent MEA	B6
VX	OPAB	B7

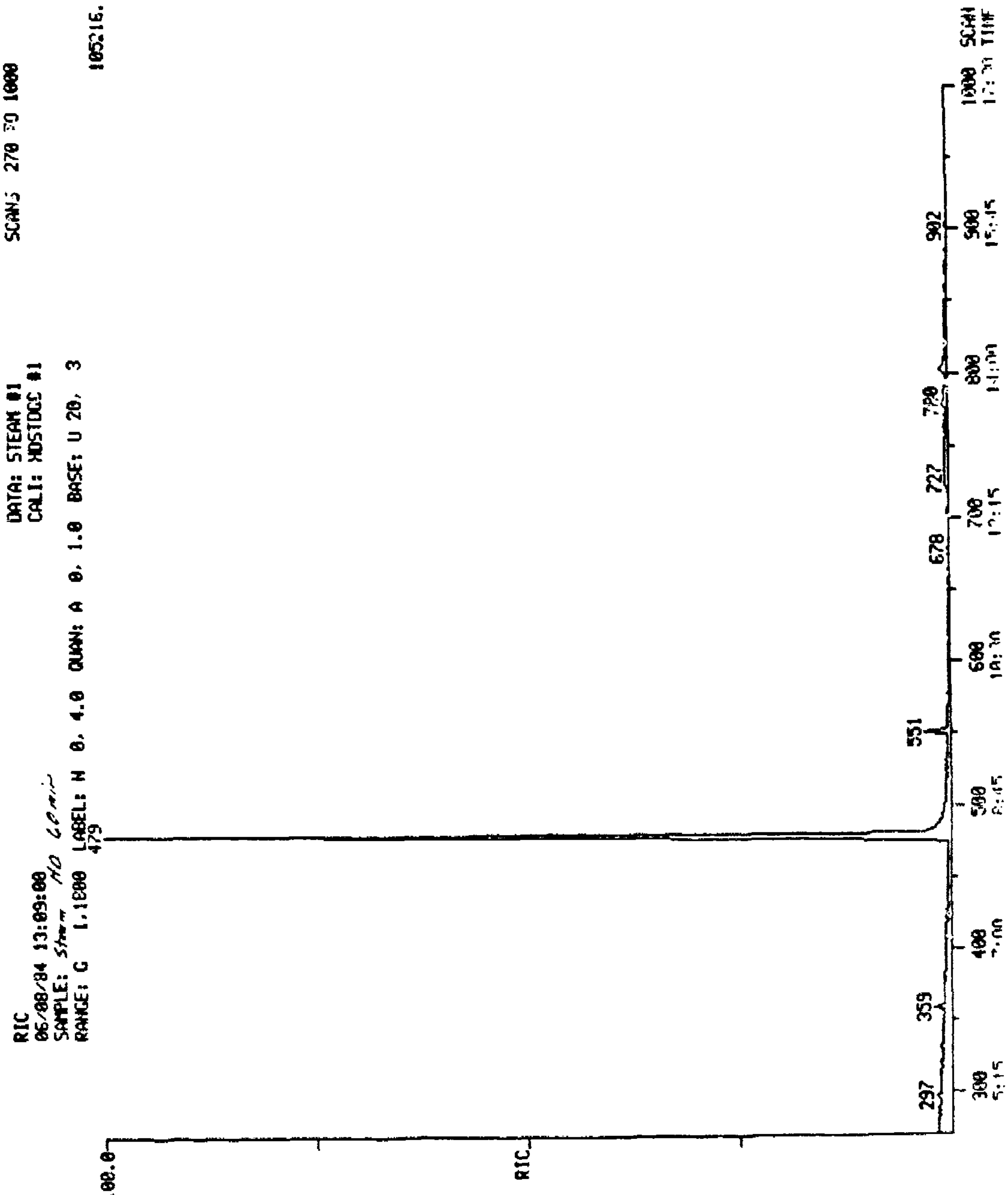

FIGURE B1. GAS CHROMATOGRAM OF EXTRACT FROM STEAM DECONTAMINATION OF HD

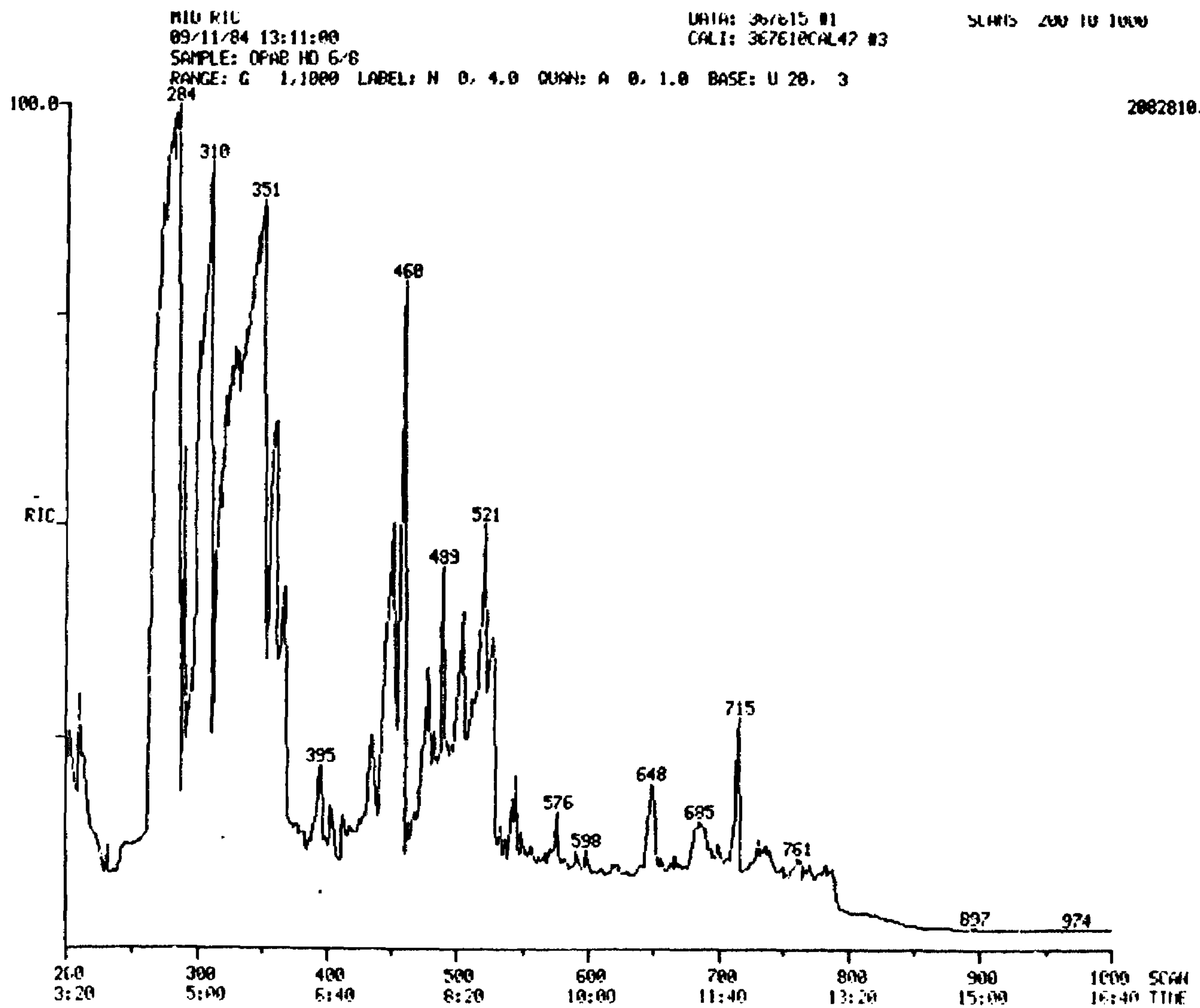

FIGURE B2. GAS CHROMATOGRAM OF EXTRACT FROM OPAB DECONTAMINATION OF HD

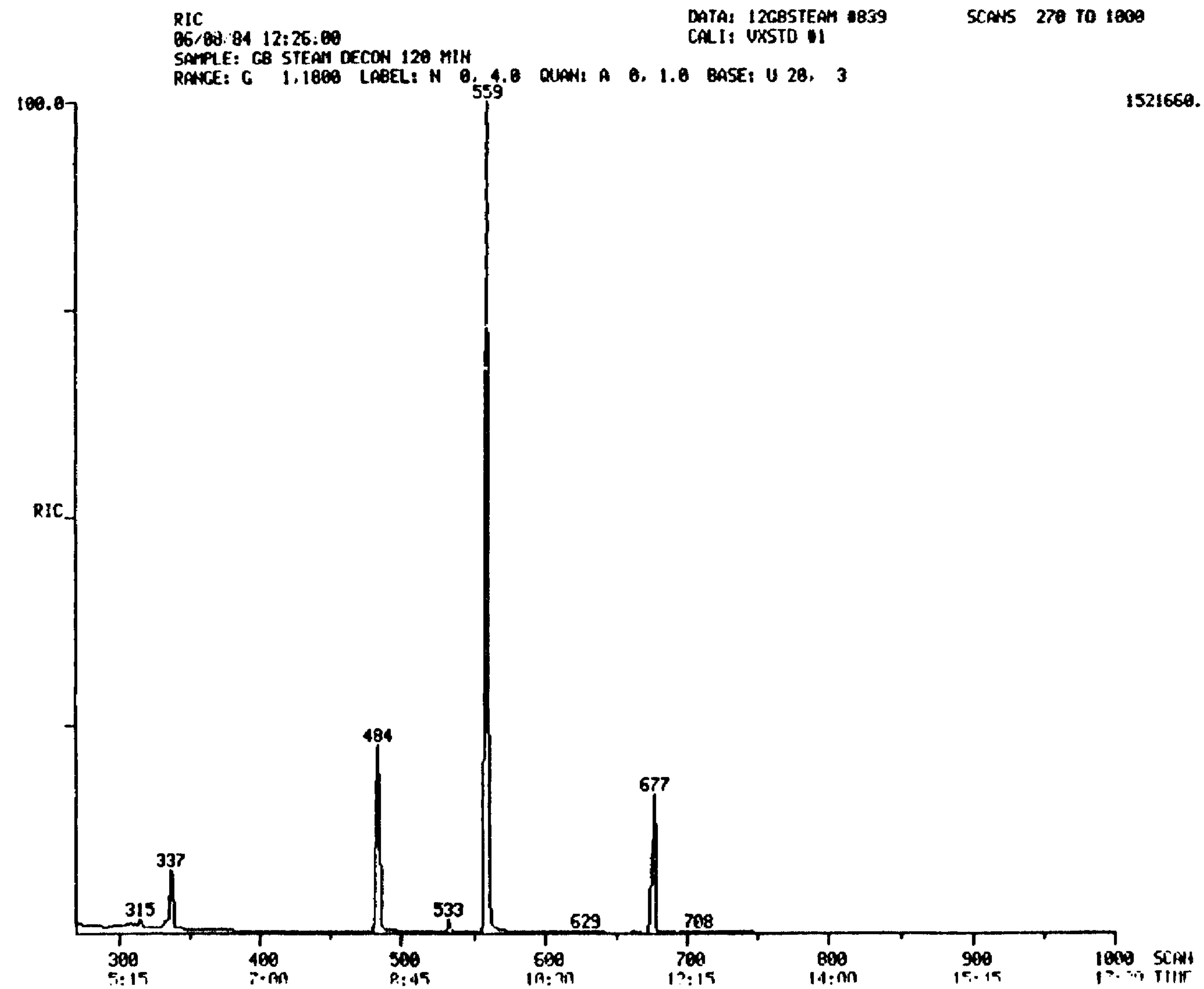

FIGURE B3. GAS CHROMATOGRAM OF EXTRACT FROM STEAM DECONTAMINATION OF GB

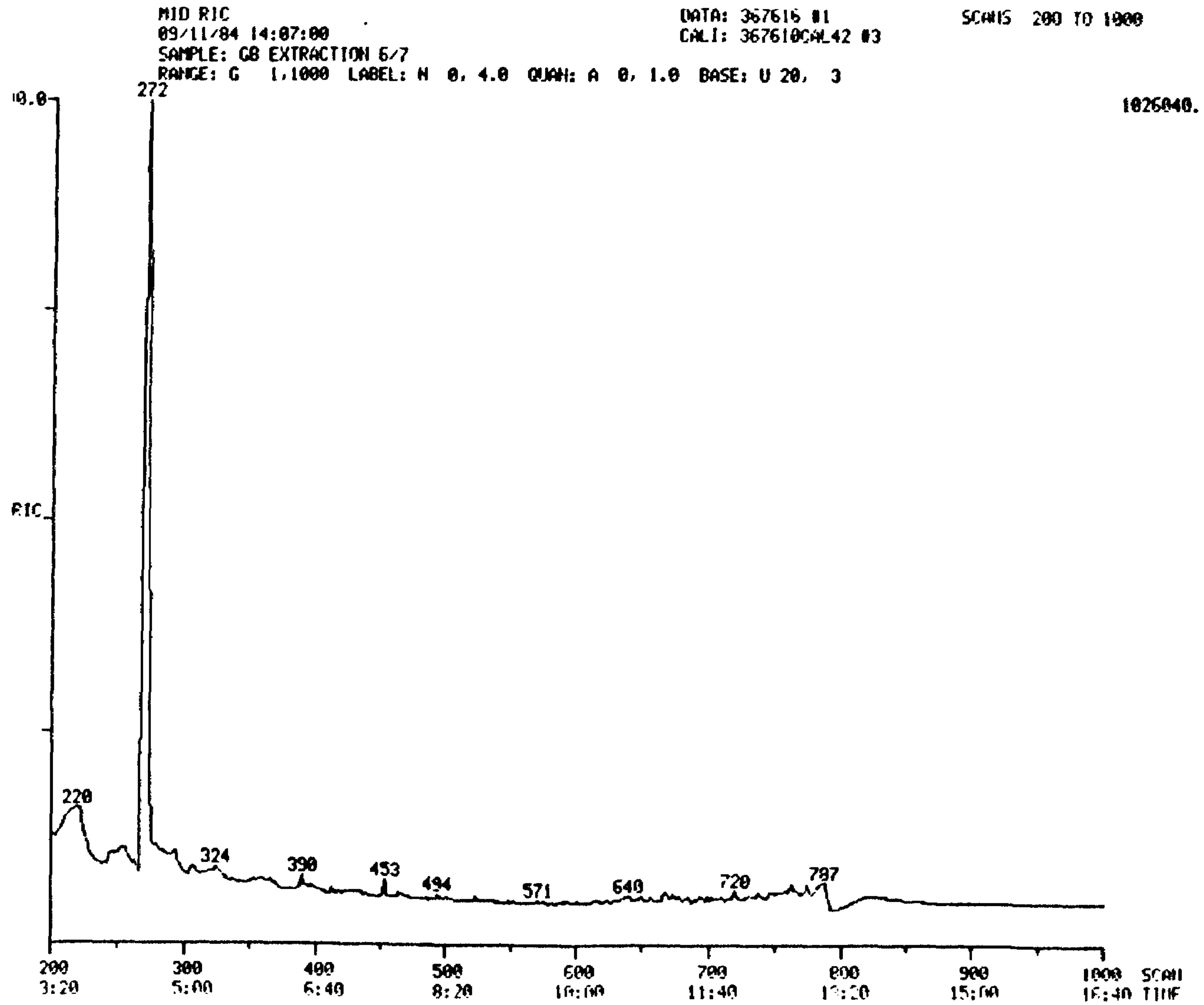

FIGURE B4. GAS CHROMATOGRAM OF EXTRACT FROM NH_3/STEAM DECONTAMINATION OF GB

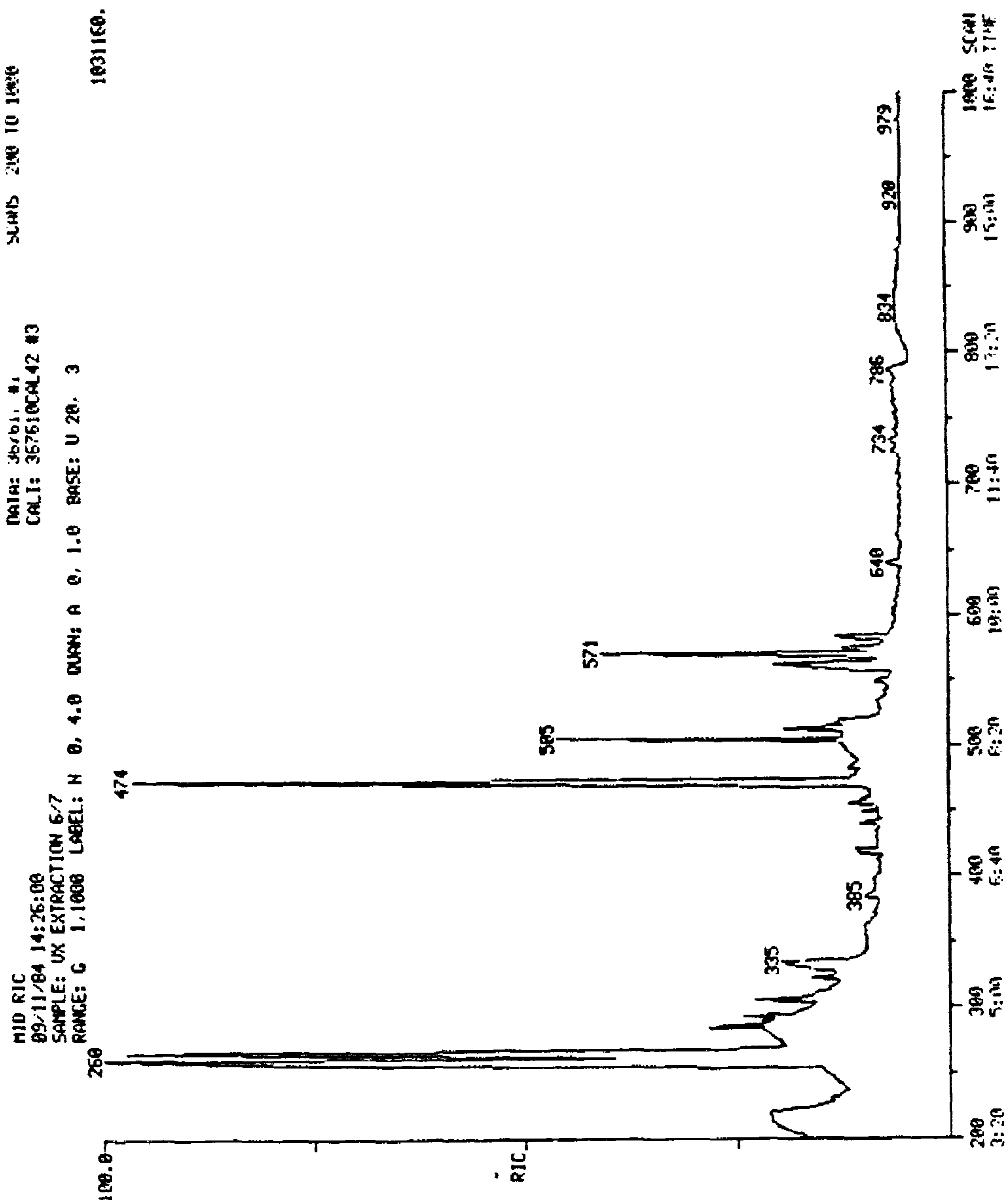

FIGURE B5. GAS CHROMATOGRAM OF EXTRACT FROM NH_3/STEAM DECONTAMINATION OF VX

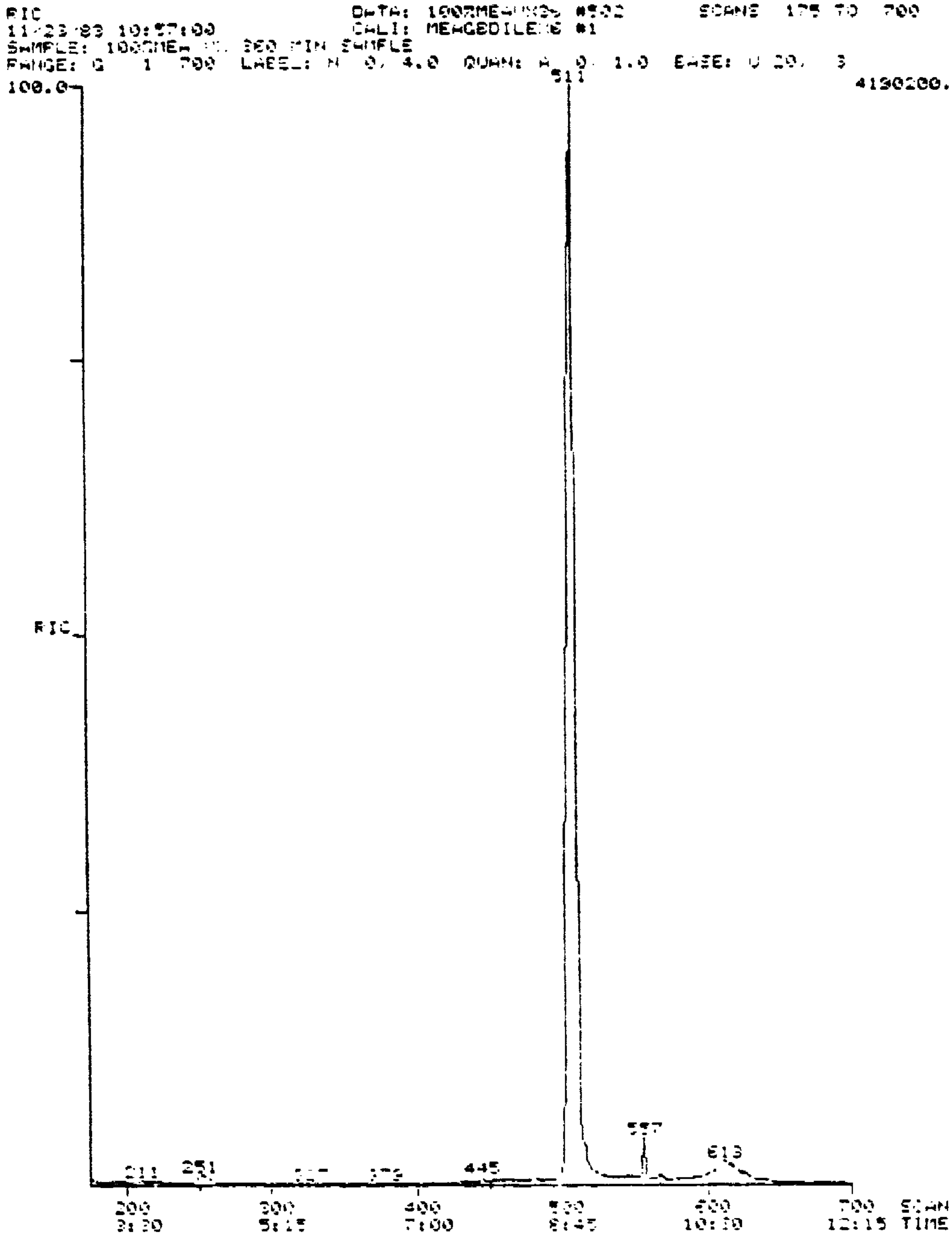

FIGURE B6. GAS CHROMATOGRAM OF EXTRACT FROM MEA (100 PERCENT) DECONTAMINATION OF VX

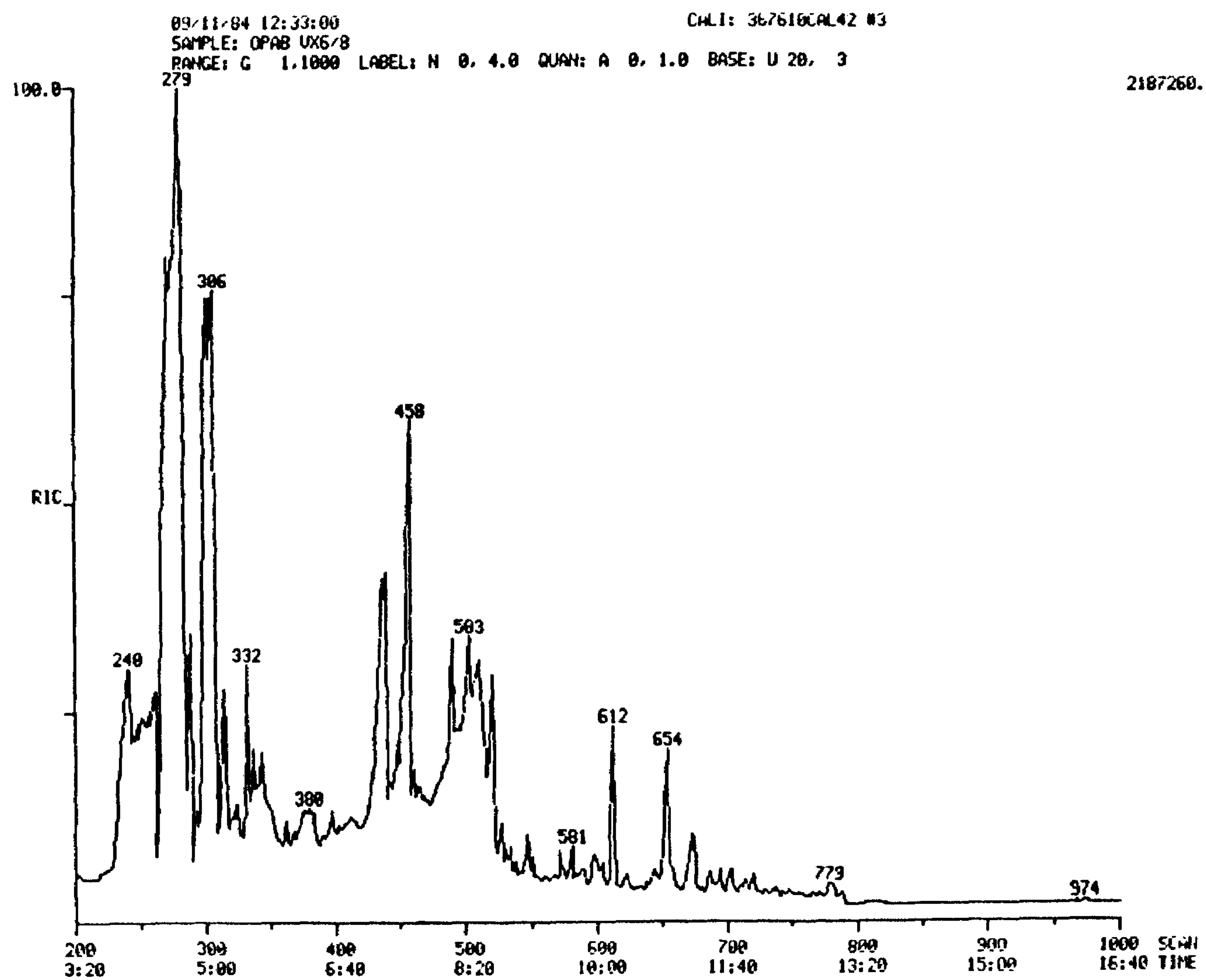

FIGURE B7. GAS CHROMATOGRAM OF EXTRACT FROM OPAB DECONTAMINATION OF VX

APPENDIX C

MASS SPECTRA

APPENDIX C

MASS SPECTRA

The following mass spectra were used in either identification of agent decomposition products or confirmation for the presence of intact agent.

Agent	Decontaminant	Figure No.
HD	Steam	C1-C3
GB	Steam	C4
VX	Steam	C5
HD	OPAB*	C6
GB	OPAB**	C7-8
VX	OPAB*	C9-C10
GB	50% MEA	C11-C12
VX	100% MEA	C13
GB	NH_3/Steam	C14
VX	NH_3/Steam	C15-C17
VX	NH_3	C18-C21

* BCL-OPAB (neat OPAB dissolved in water)

** BF-OPAB (sodium salt of OPAB and additives dissolved in water)

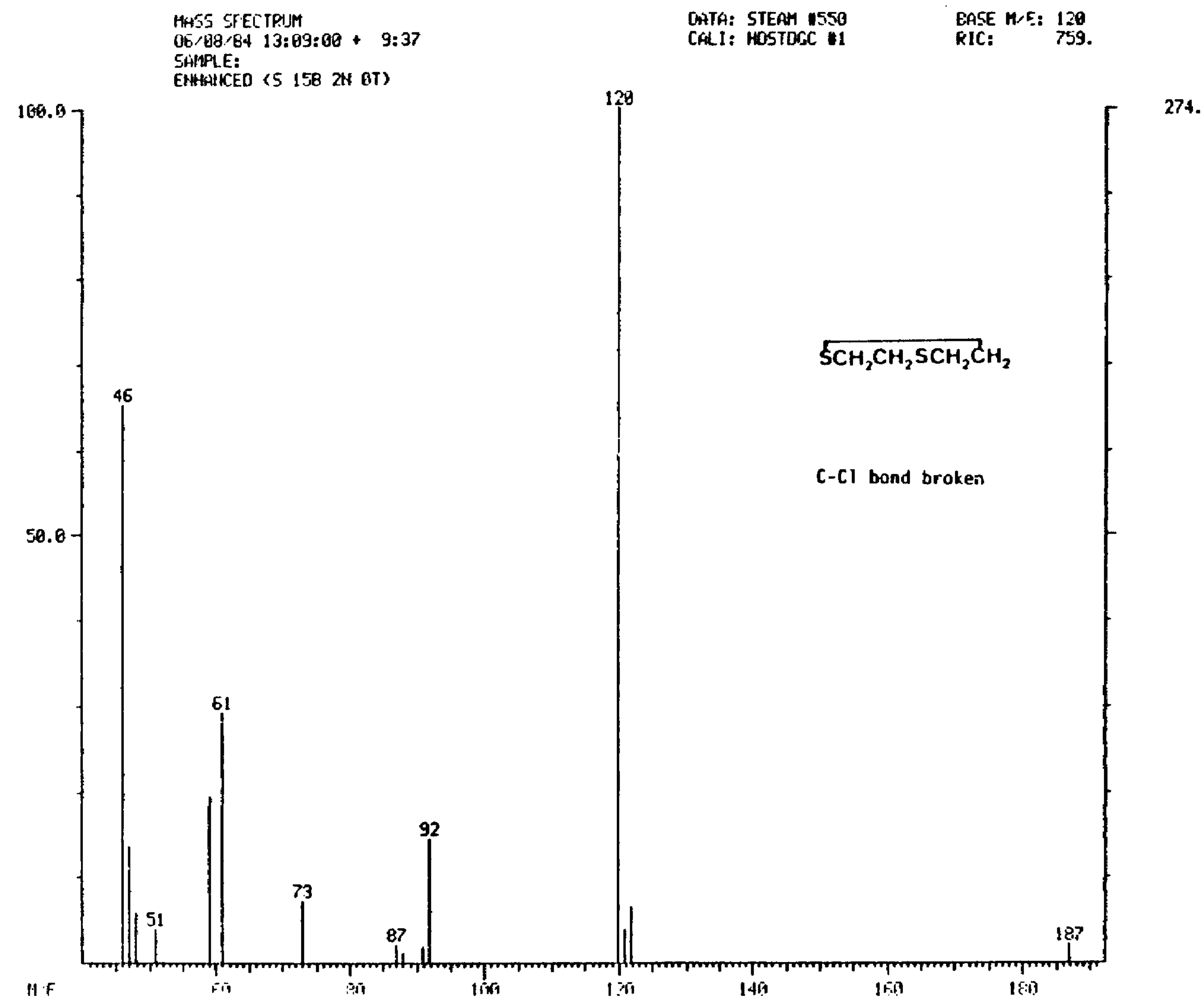

FIGURE C1. MASS SPECTRUM OF EXTRACT FROM STEAM DECONTAMINATION OF HD (#1)

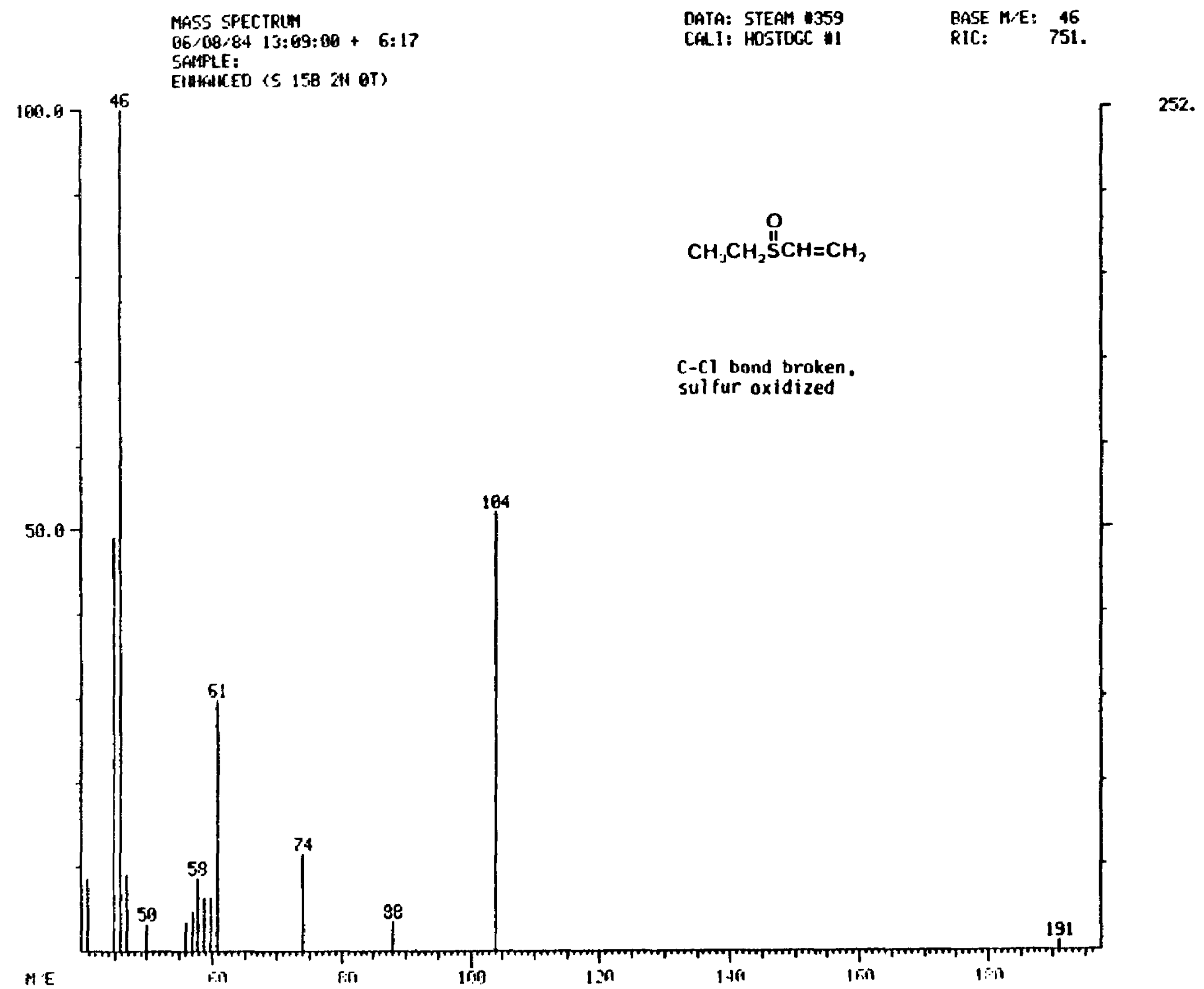

FIGURE C2. MASS SPECTRUM OF EXTRACT FROM STEAM DECONTAMINATION OF HD (#2)

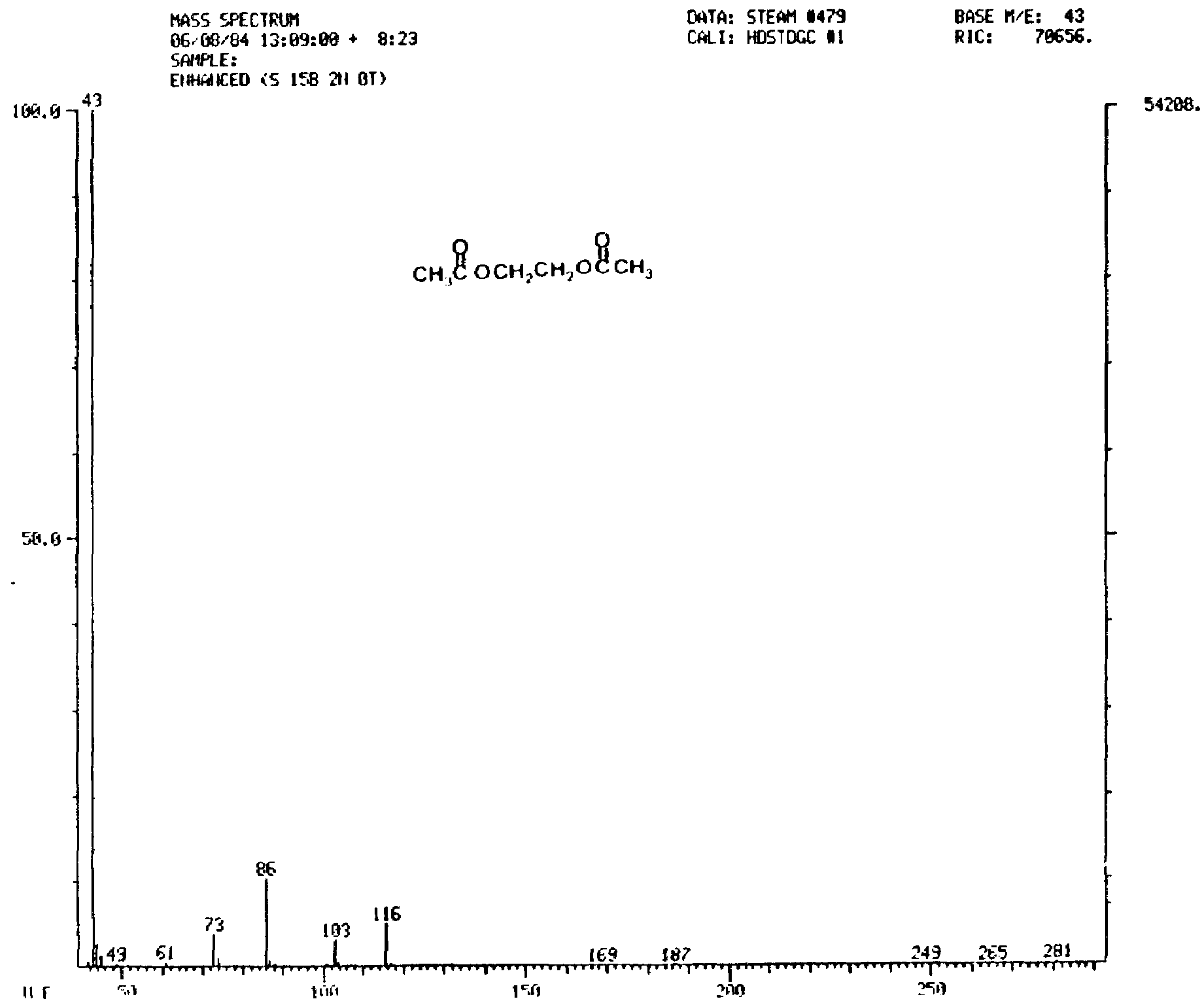

FIGURE C3. MASS SPECTRUM OF EXTRACT FROM STEAM DECONTAMINATION OF HD (#3)

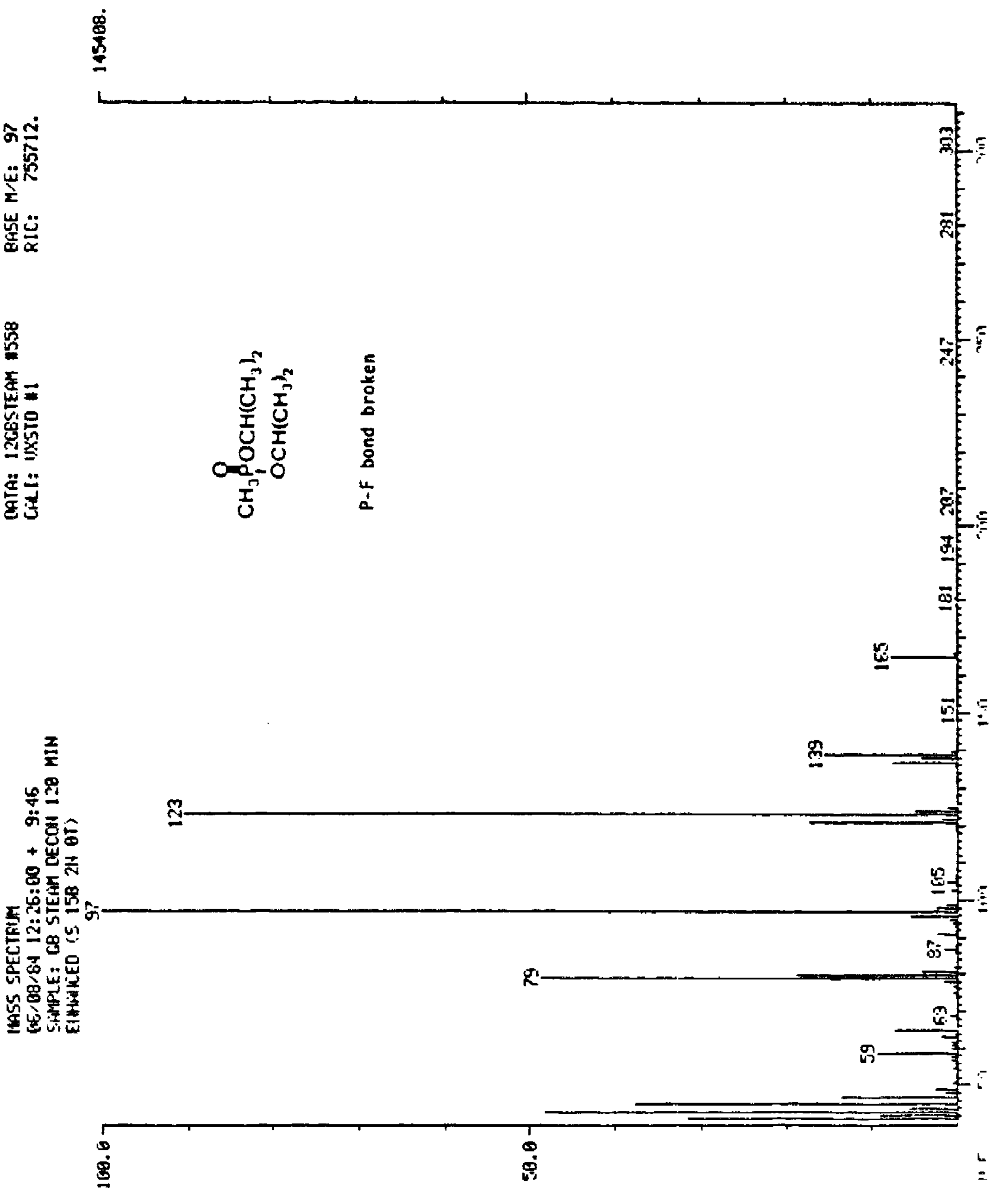

FIGURE C4. MASS SPECTRUM OF EXTRACT FROM STEAM DECONTAMINATION OF GB

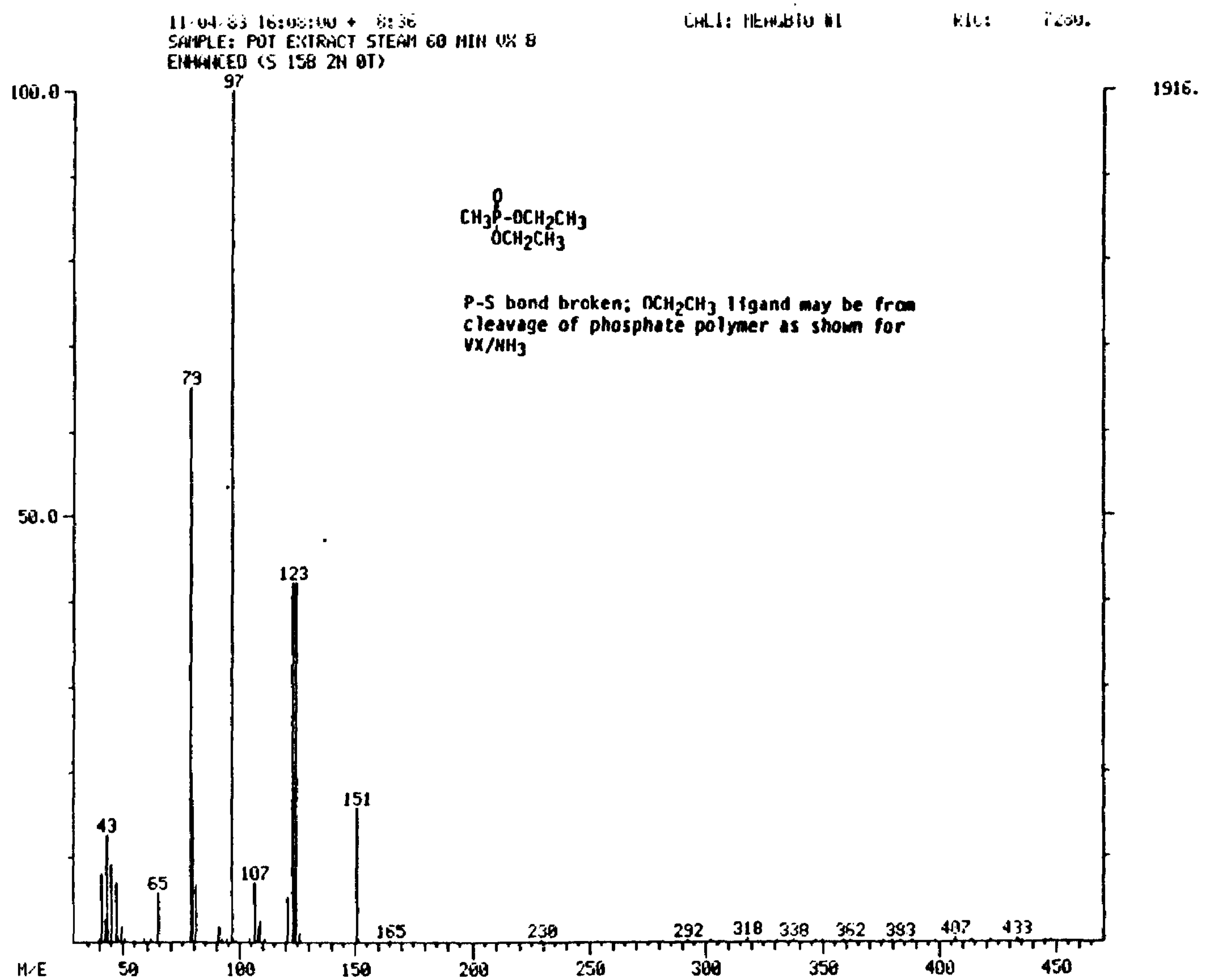

FIGURE C5. MASS SPECTRUM OF EXTRACT FROM STEAM DECONTAMINATION OF VX

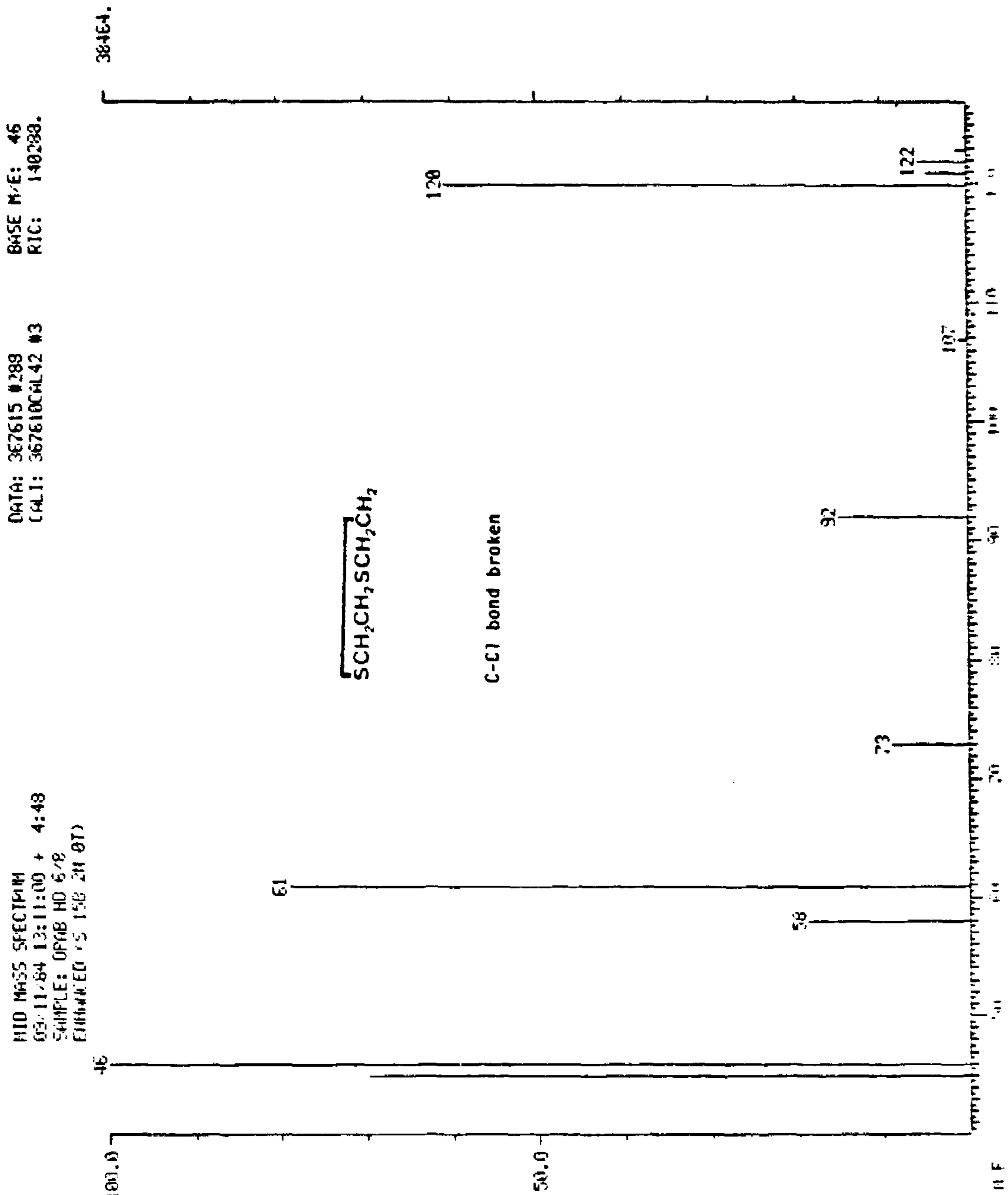

FIGURE C6. MASS SPECTRUM OF EXTRACT FROM OPAB DECONTAMINATION OF HD

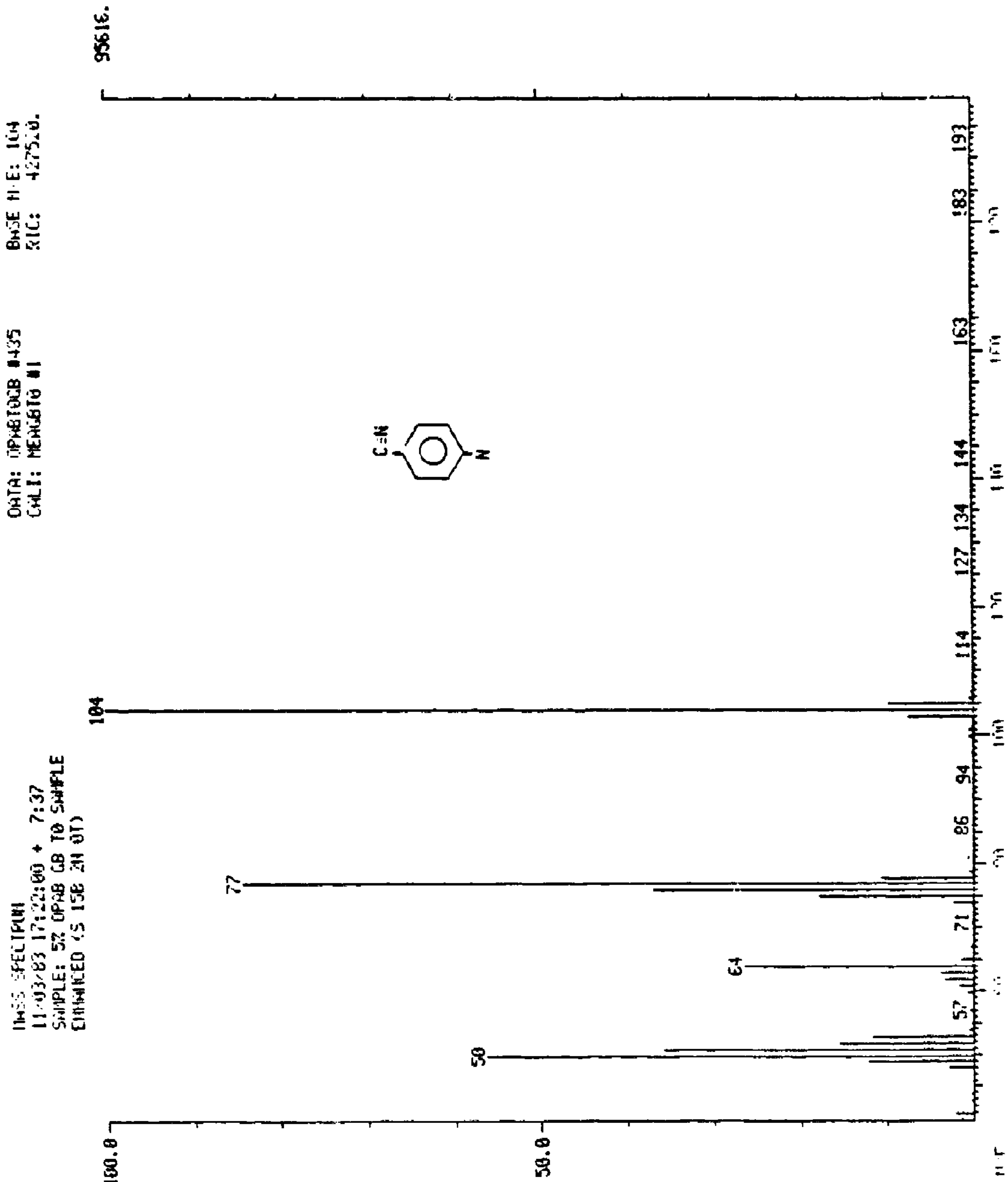

FIGURE C7. MASS SPECTRUM OF EXTRACT FROM OPAB DECONTAMINATION OF GB (#1)

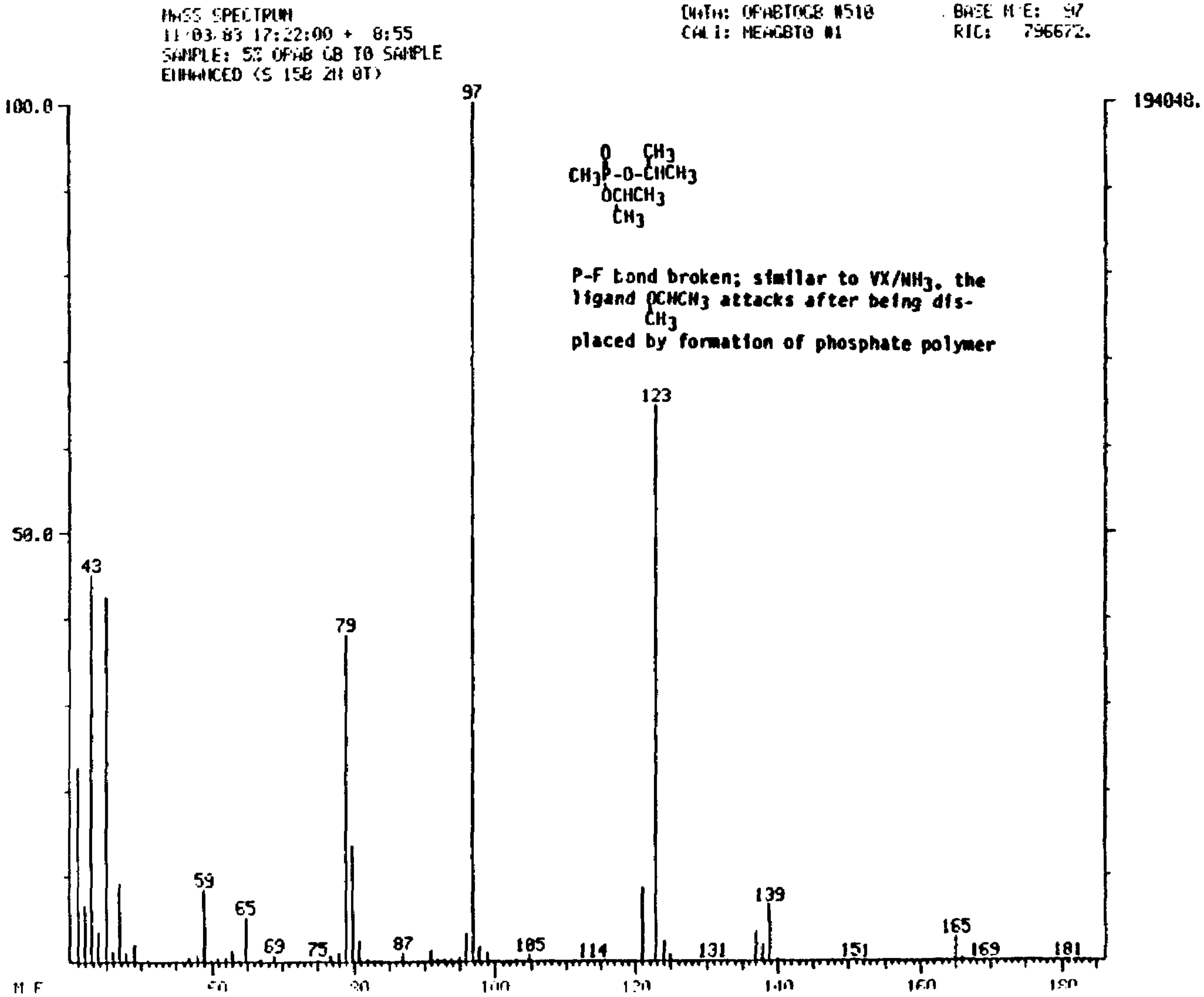

FIGURE C8. MASS SPECTRUM OF EXTRACT FROM OPAB DECONTAMINATION OF GB (#2)

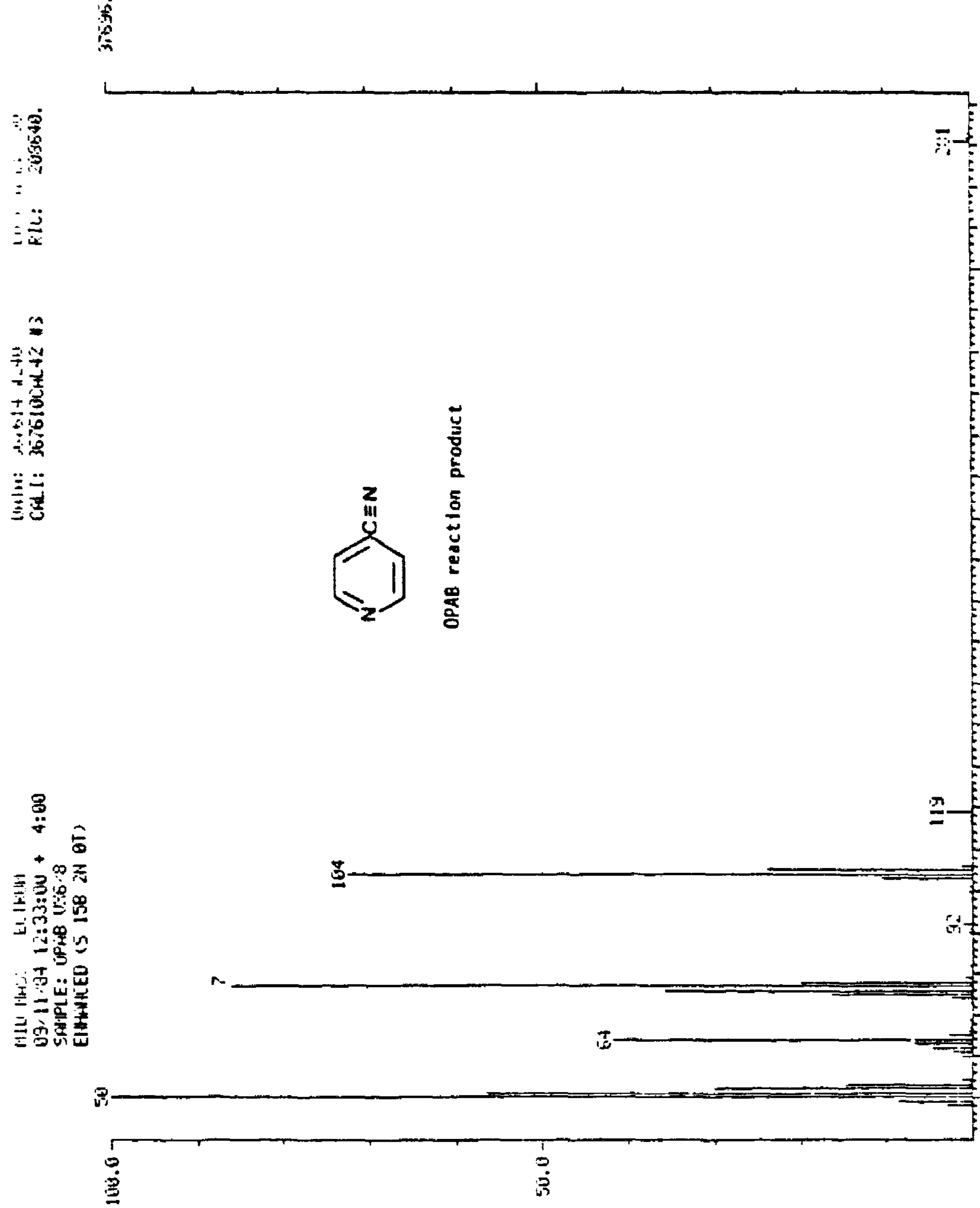

FIGURE C9. MASS SPECTRUM OF EXTRACT FROM OPAB DECONTAMINATION OF VX (#1)

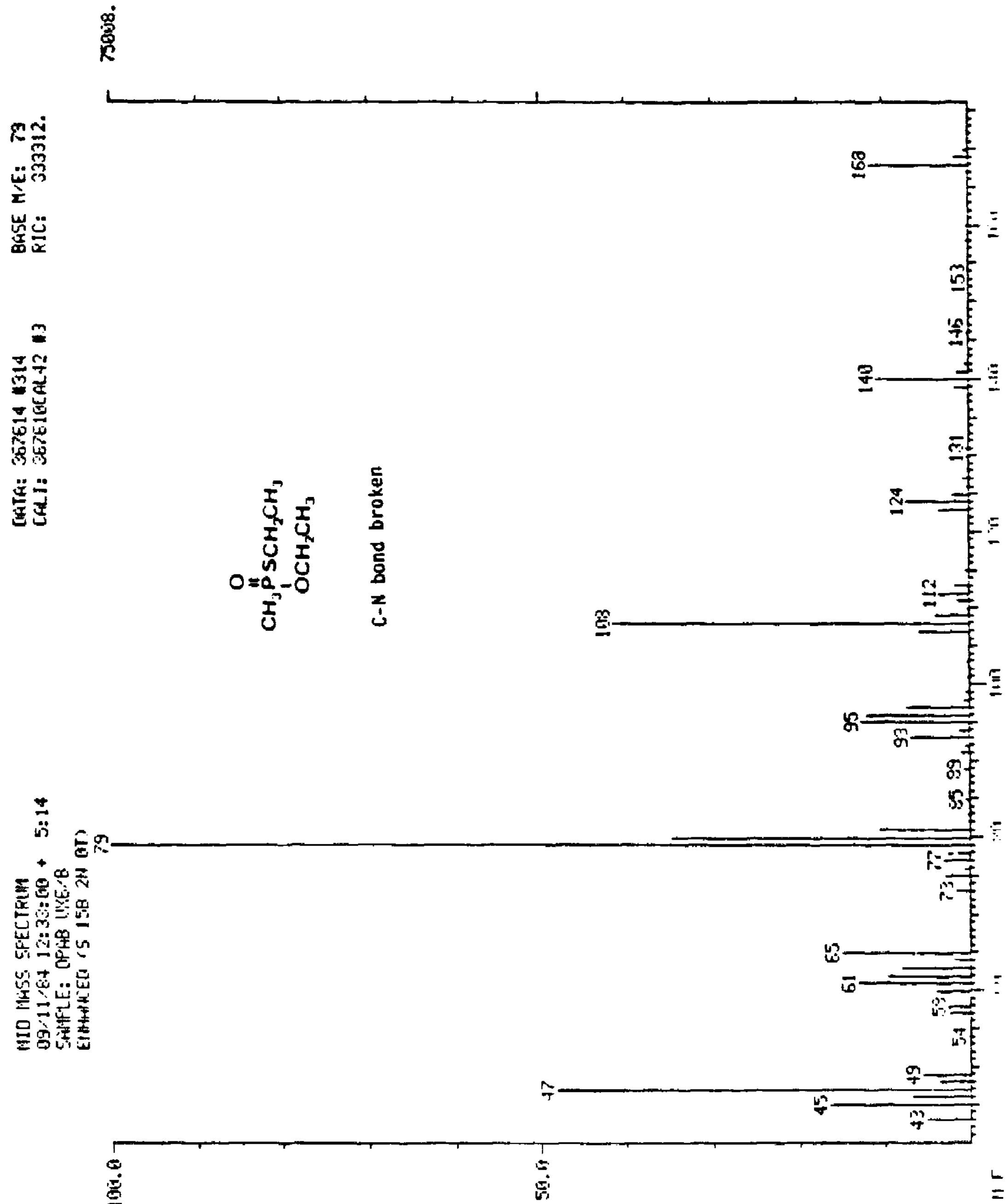

FIGURE C10. MASS SPECTRUM OF EXTRACT FROM OPAB DECONTAMINATION OF VX (#2)

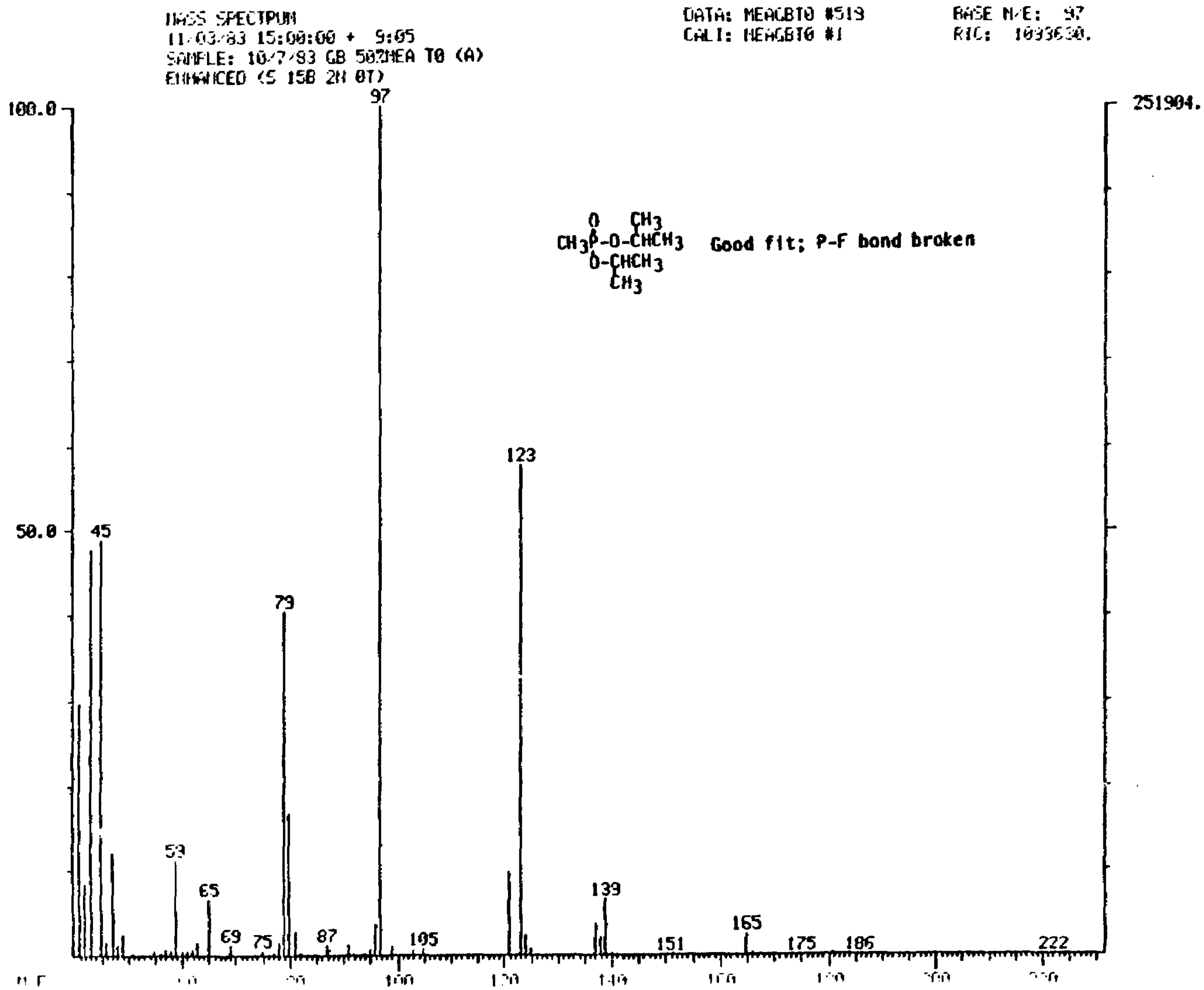

FIGURE C11. MASS SPECTRUM OF EXTRACT FROM MEA (50 PERCENT) DECONTAMINATION OF GB (#1)

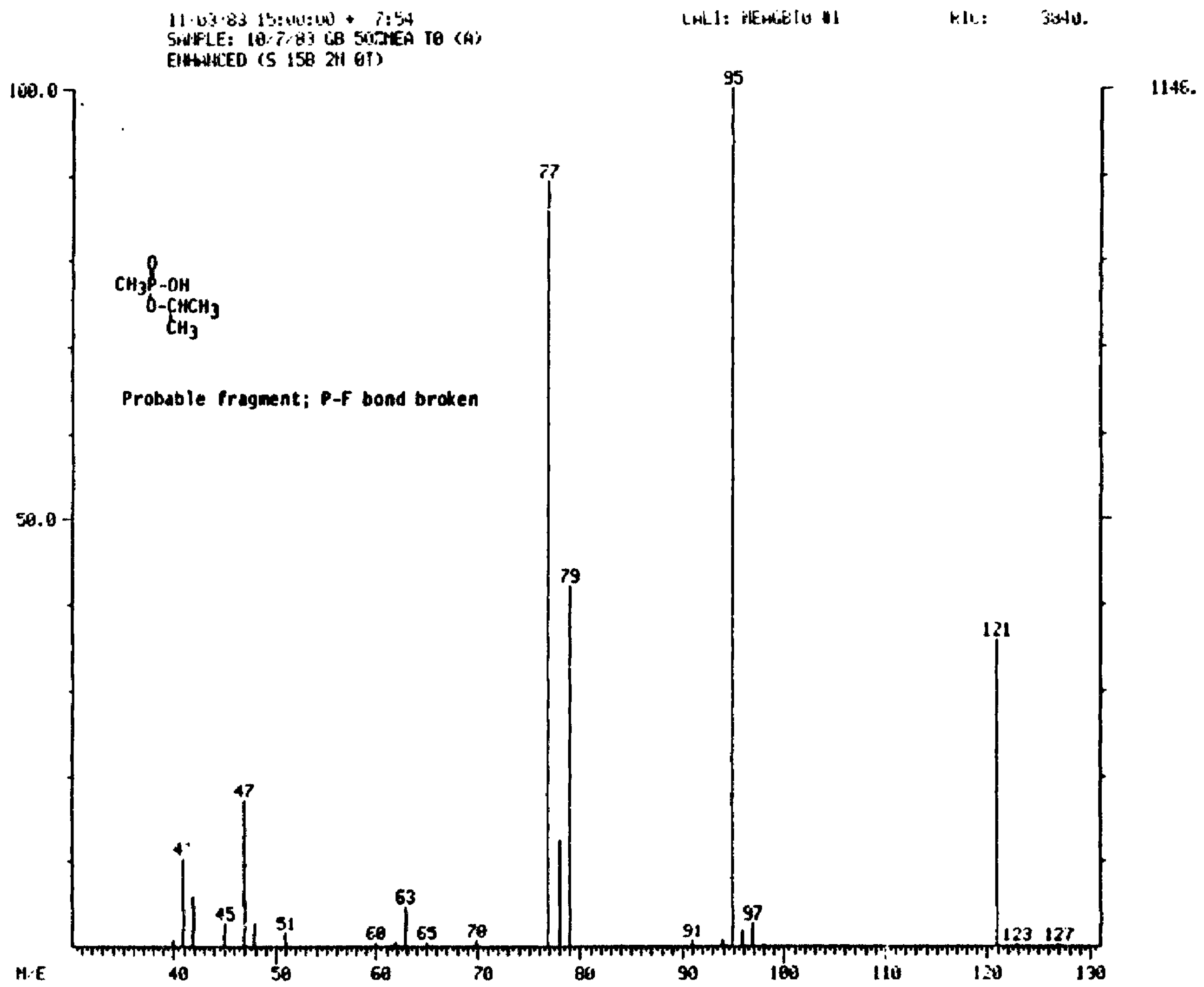

FIGURE C12. MASS SPECTRUM OF EXTRACT FROM MEA (50 PERCENT) DECONTAMINATION OF GB (#2)

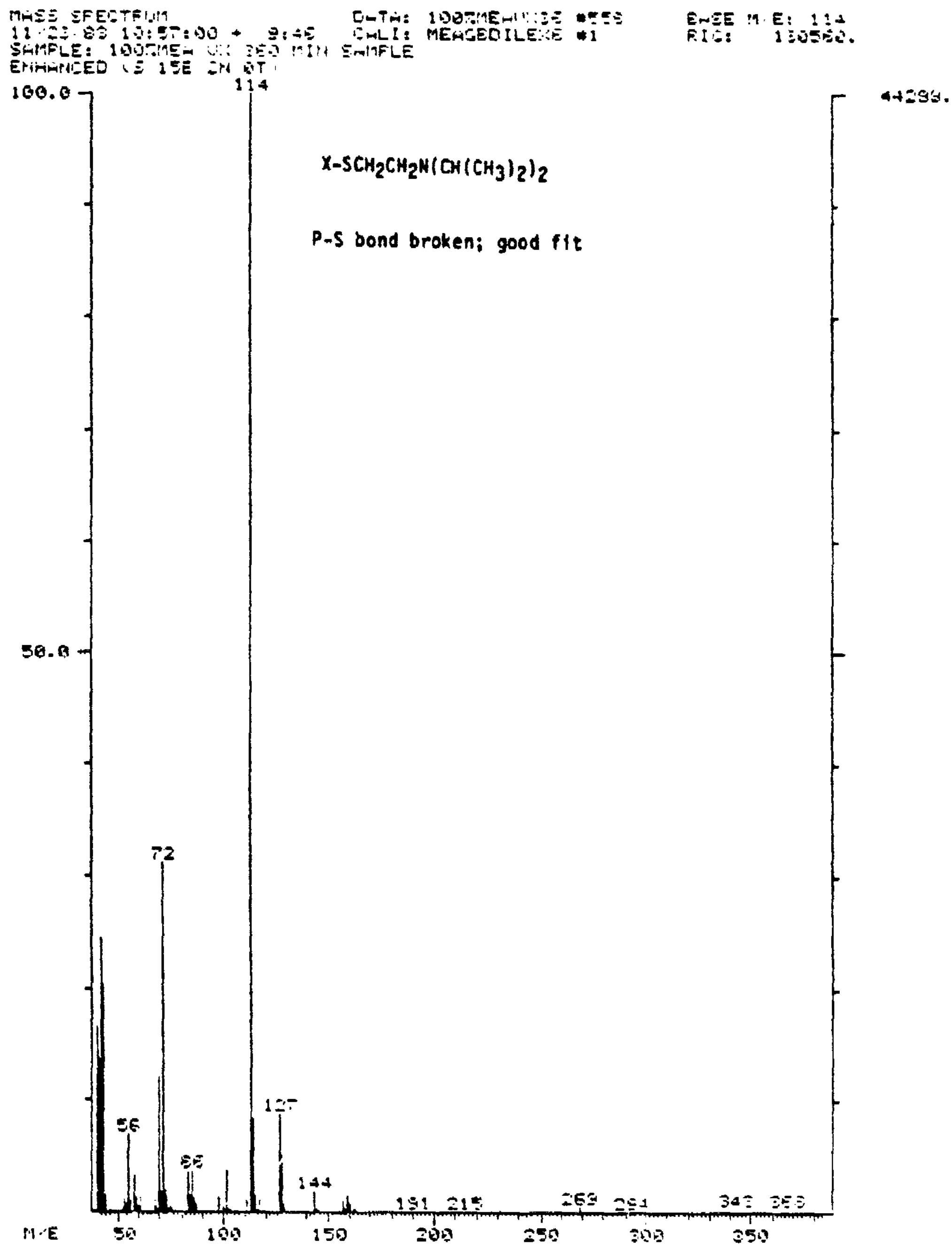

FIGURE C13. MASS SPECTRUM OF EXTRACT FROM MEA (100 PERCENT) DECONTAMINATION OF VX

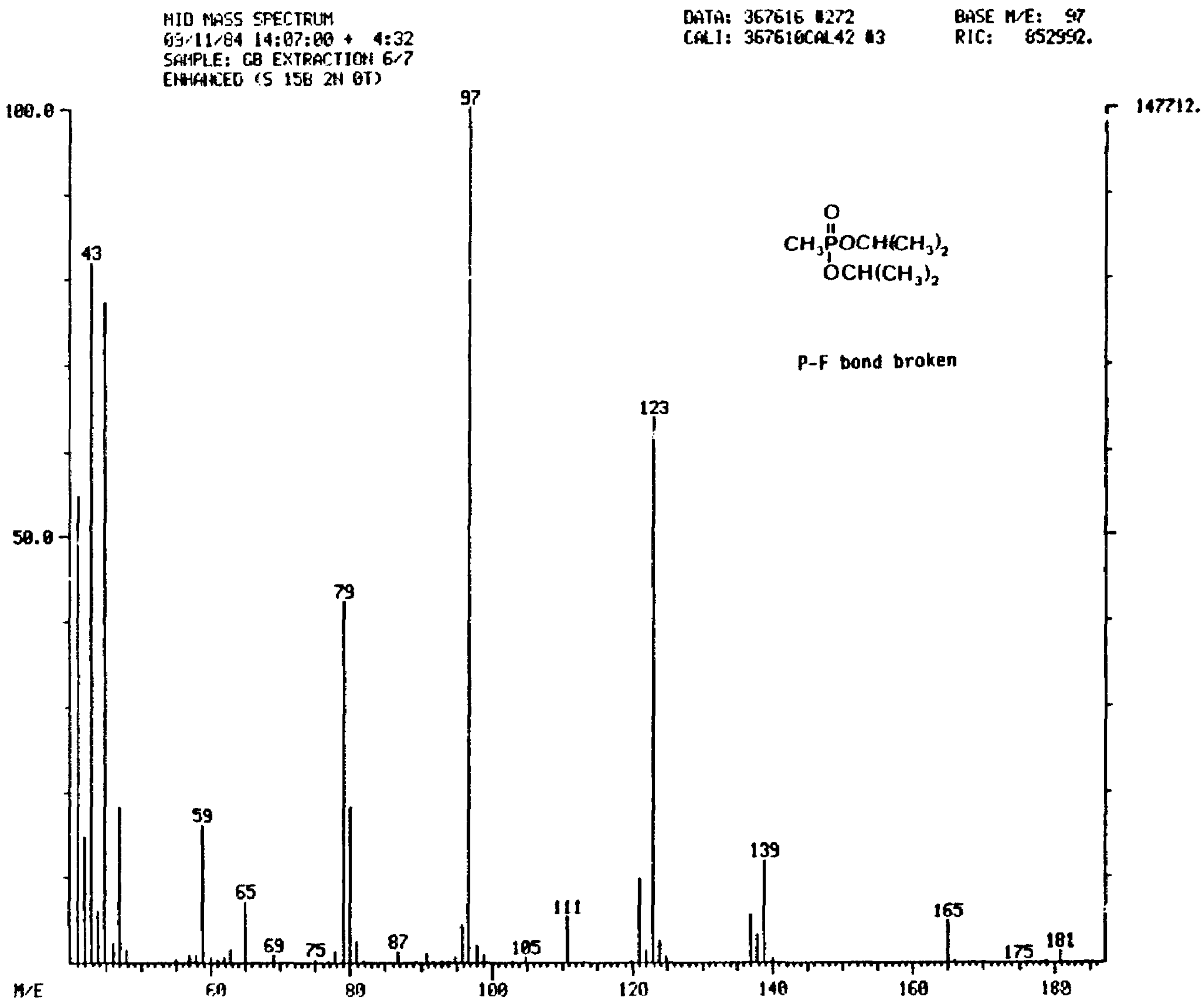

FIGURE C14. MASS SPECTRUM OF EXTRACT FROM NH_3/STEAM DECONTAMINATION OF GB

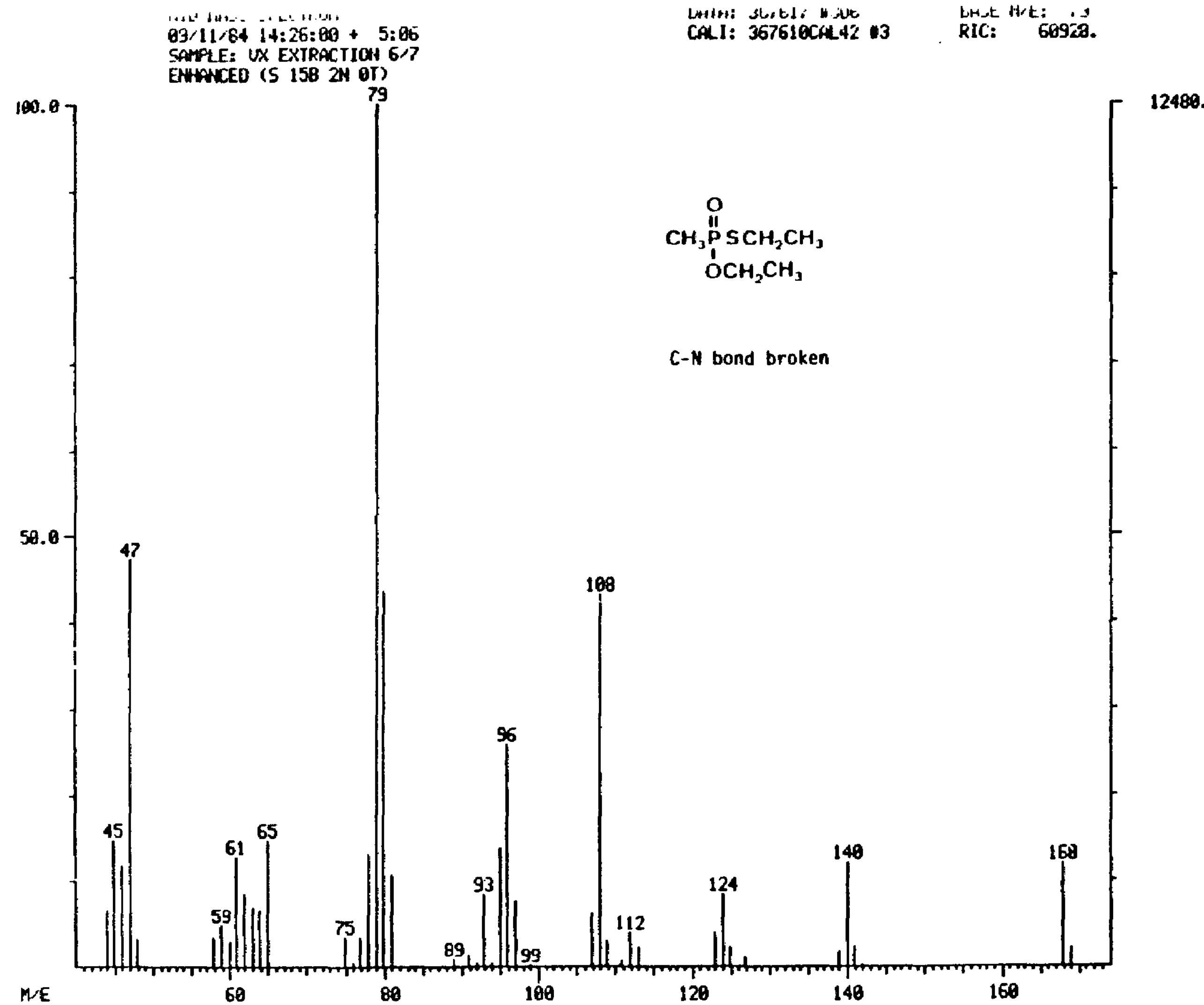

FIGURE C15. MASS SPECTRUM OF EXTRACT FROM NH_3/STEAM DECONTAMINATION OF VX (#1)

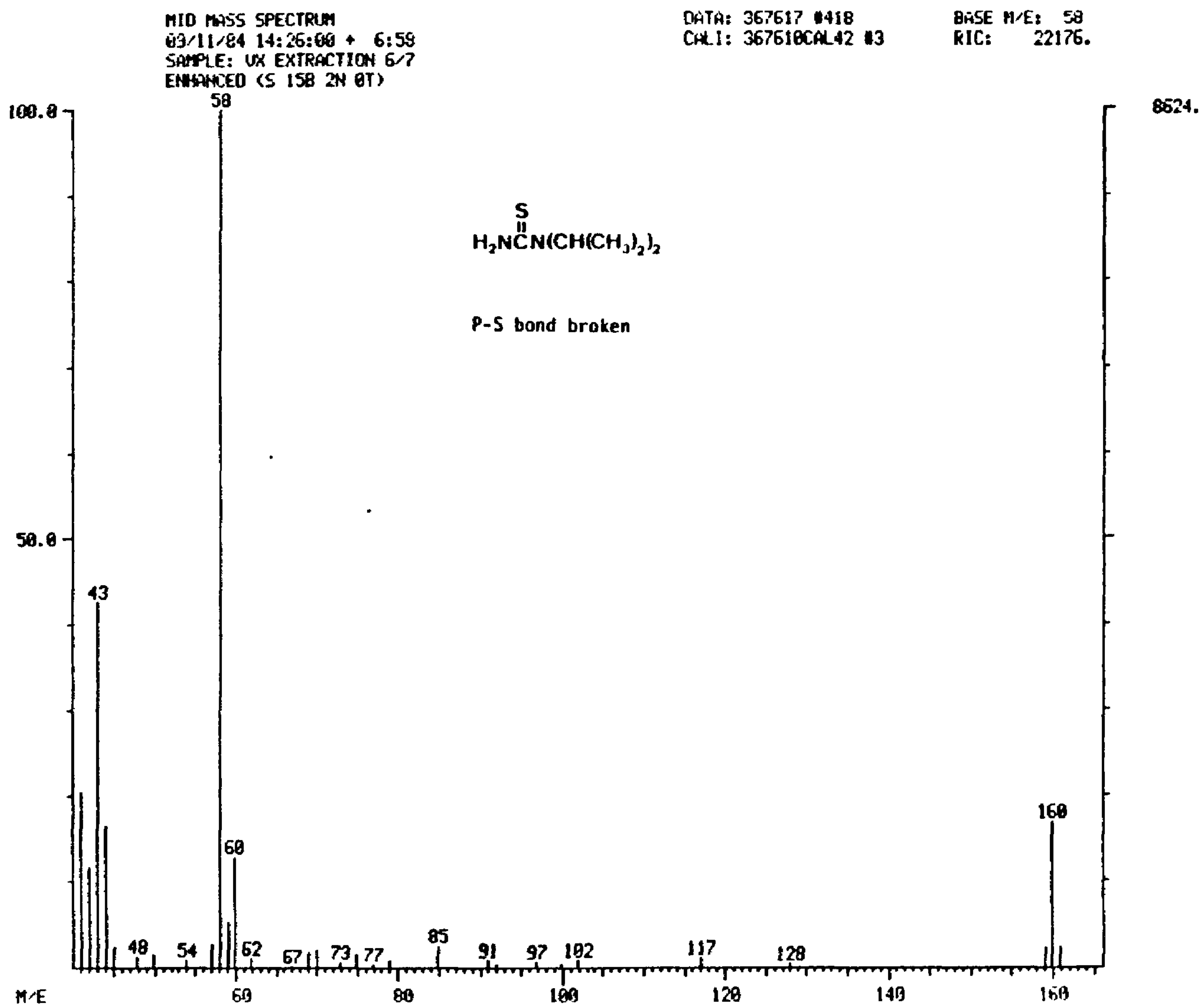

FIGURE C16. MASS SPECTRUM OF EXTRACT FROM NH_3/STEAM DECONTAMINATION OF VX (#2)

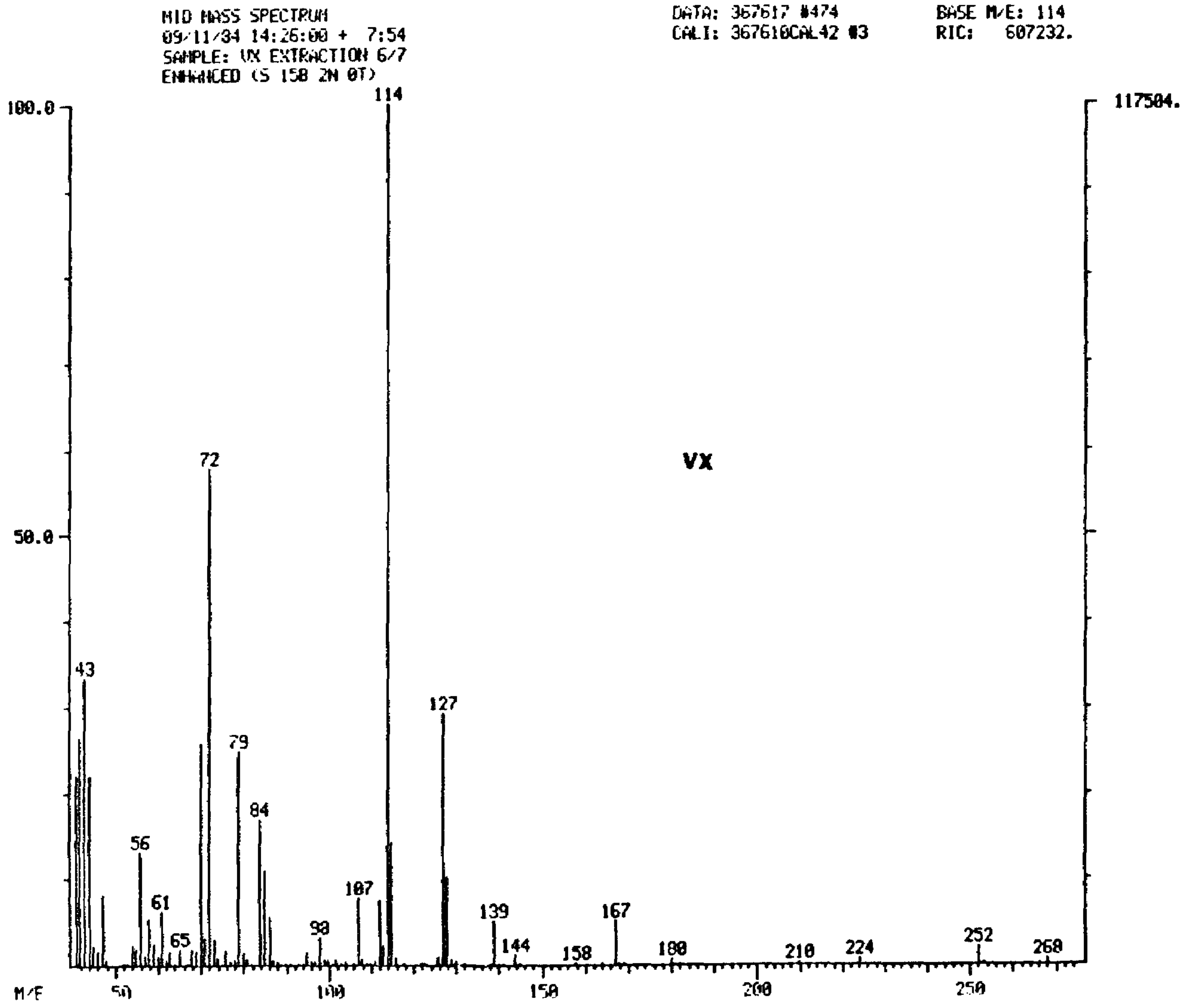

FIGURE C17. MASS SPECTRUM OF EXTRACT FROM NH_3/STEAM DECONTAMINATION OF VX (#3)

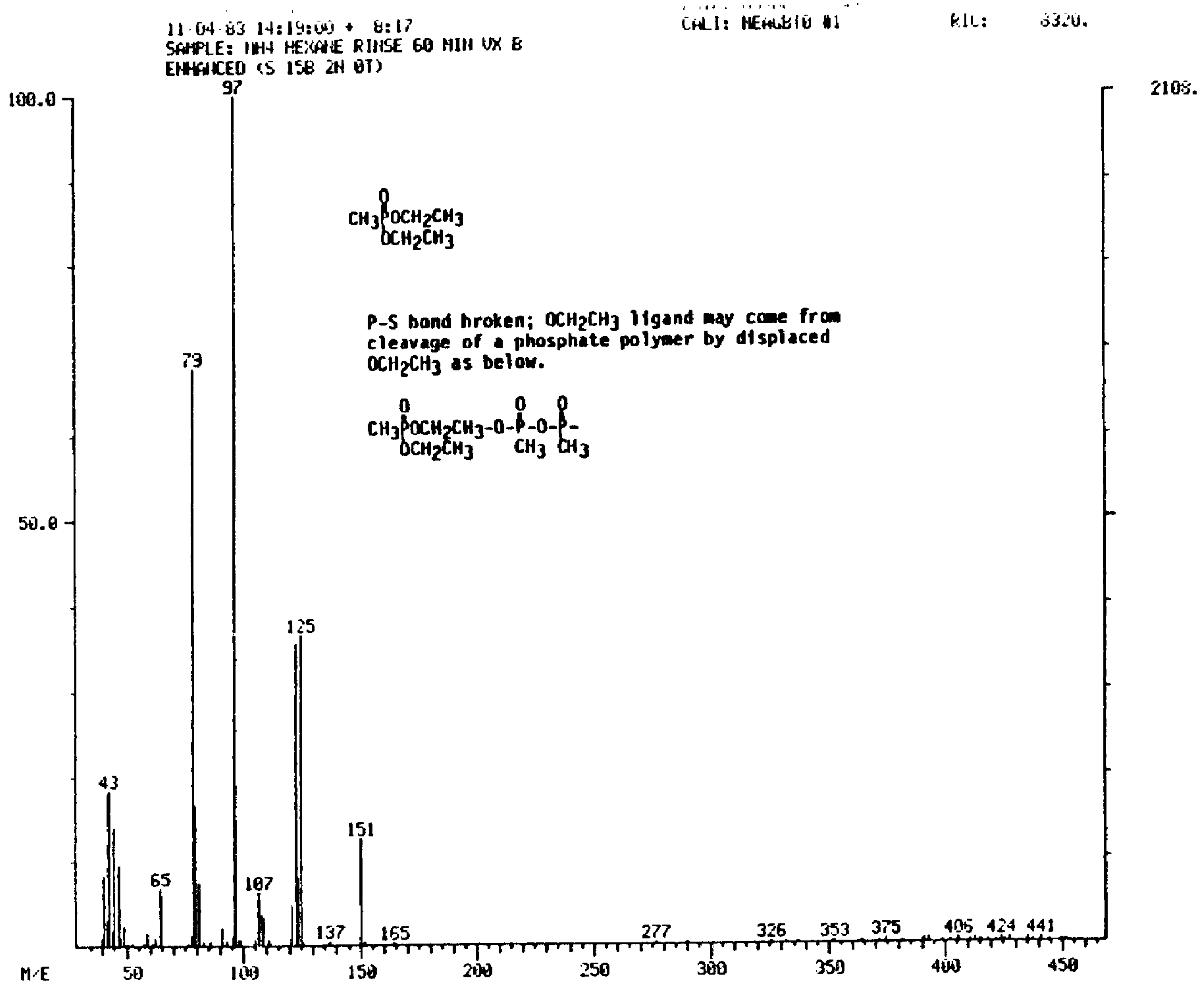

FIGURE C18. MASS SPECTRUM OF EXTRACT FROM NH_3 DECONTAMINATION OF VX (#1)

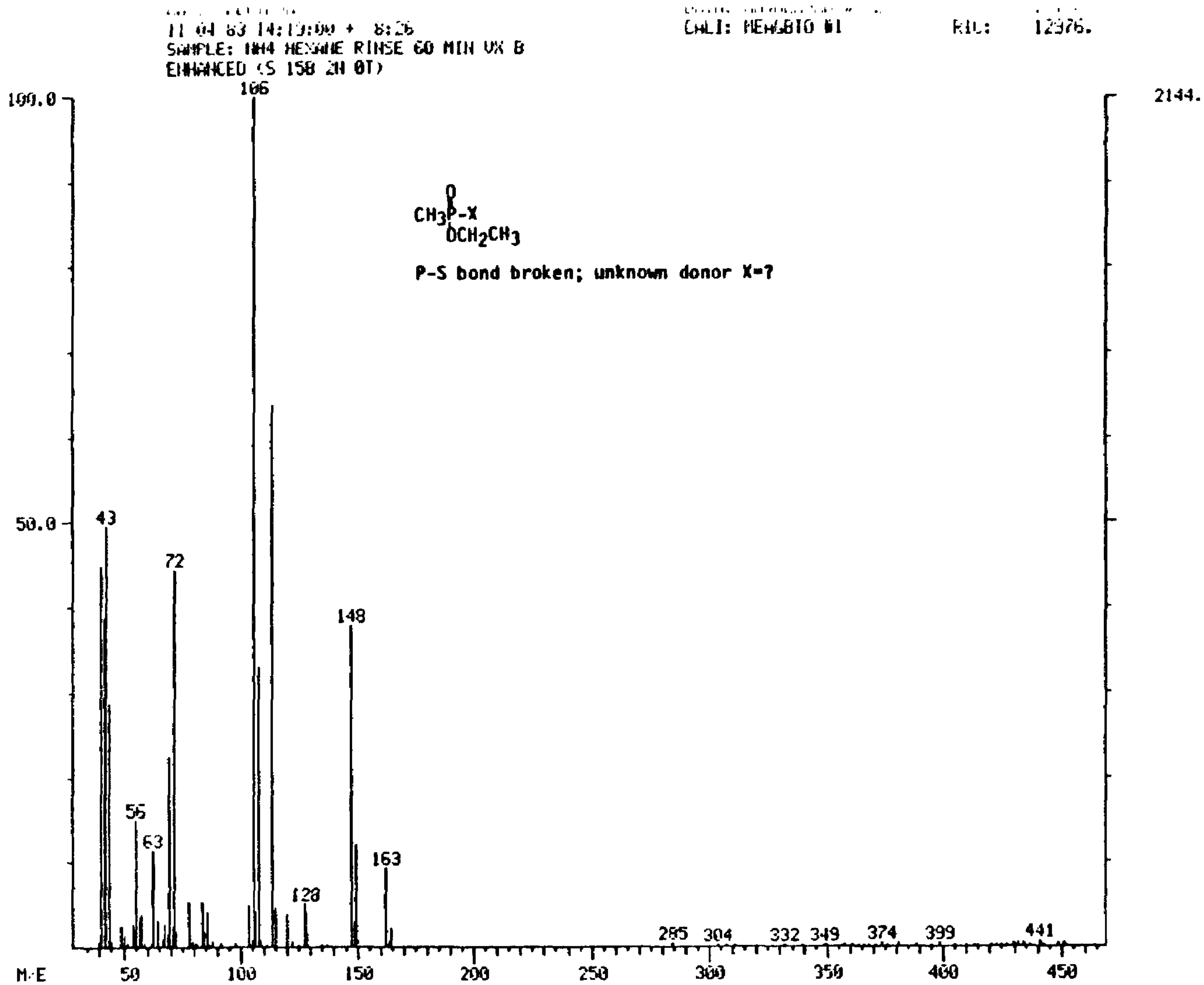

FIGURE C19. MASS SPECTRUM OF EXTRACT FROM NH_3 DECONTAMINATION OF VX (#2)

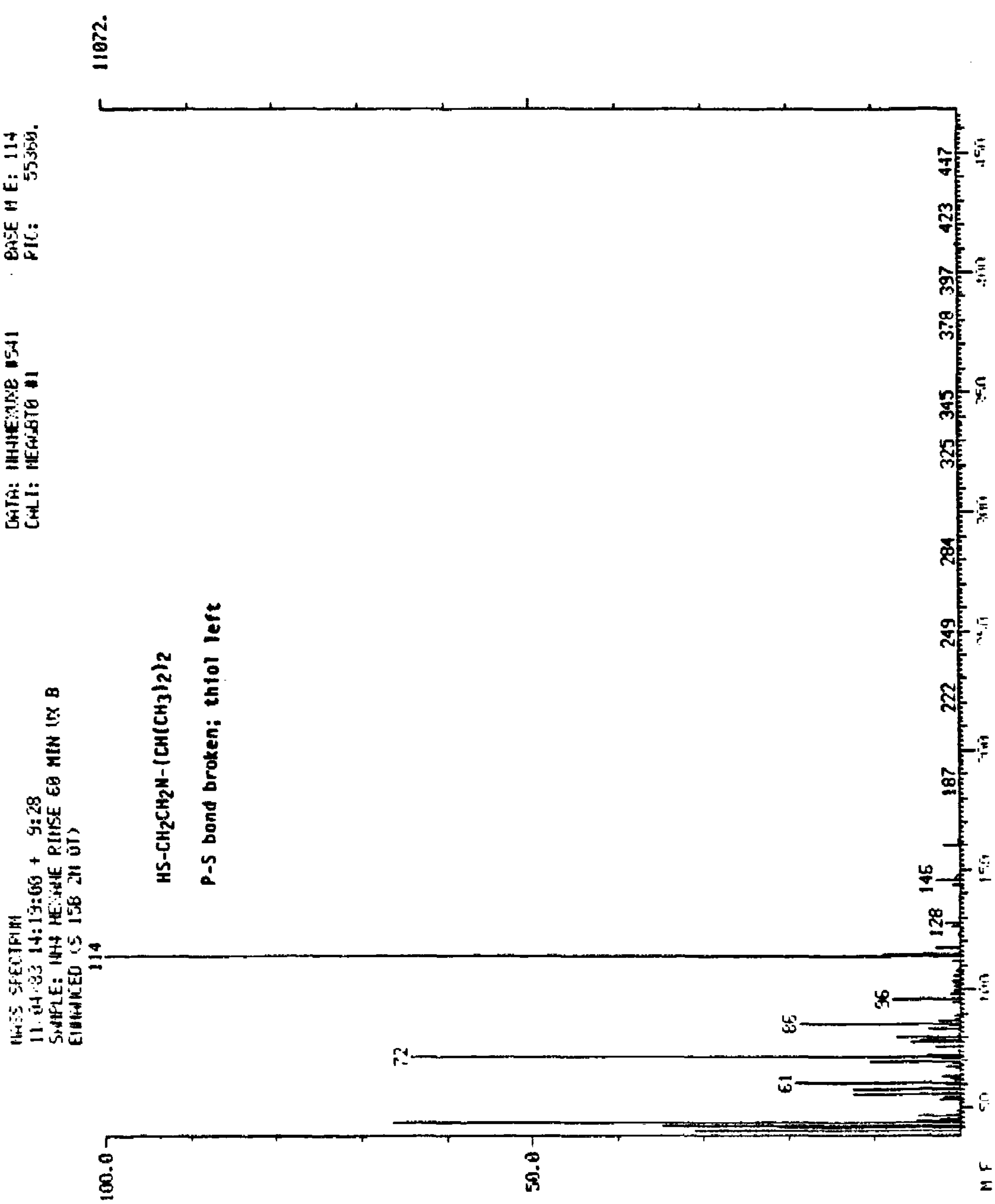

FIGURE C20. MASS SPECTRUM OF EXTRACT FROM NH_3 DECONTAMINATION OF VX (#3)

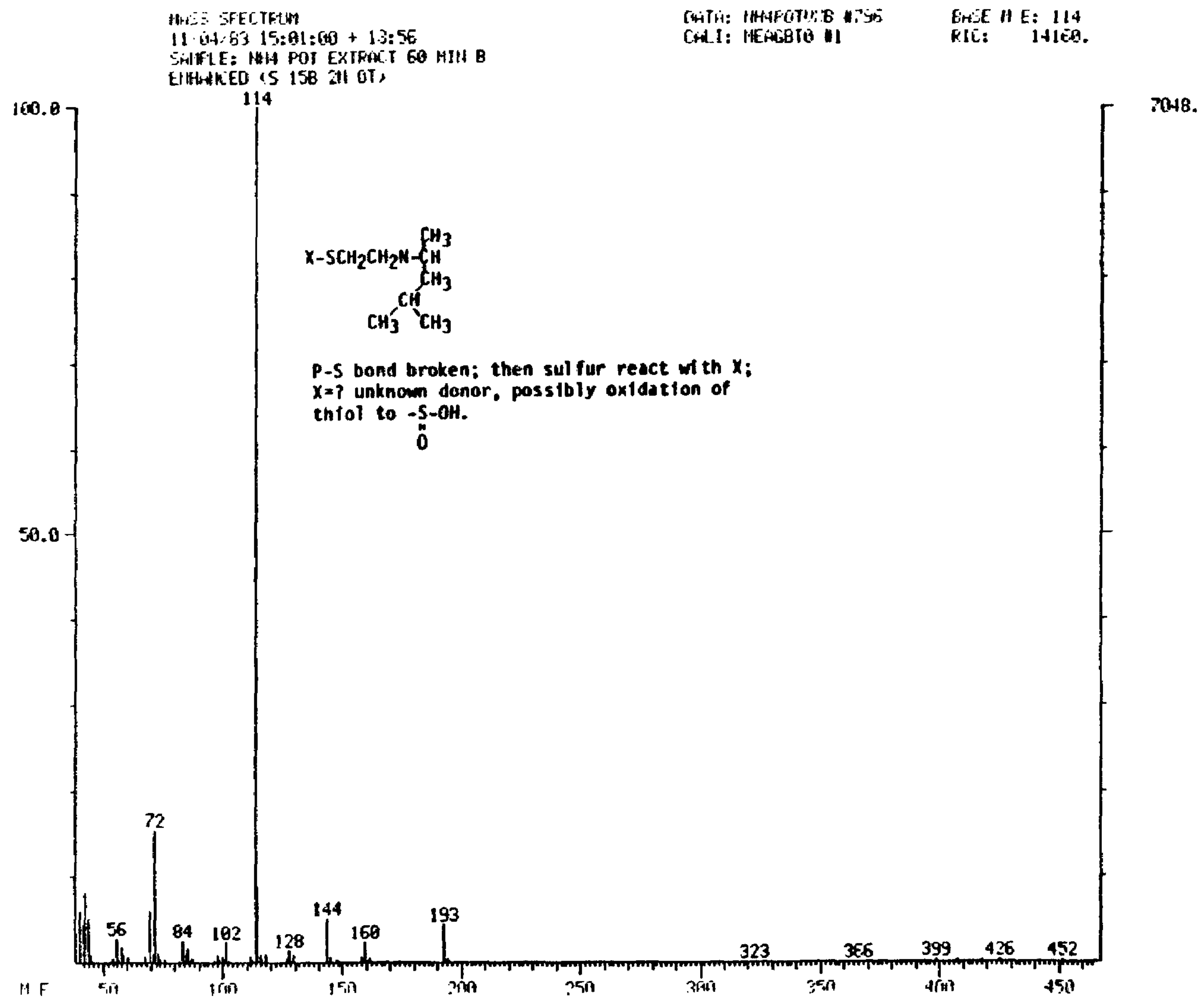

FIGURE C21. MASS SPECTRUM OF EXTRACT FROM NH_3 DECONTAMINATION OF VX (#4)

APPENDIX III

SUBTASK 4. DIFFUSION TESTS

TEST REPORT

for

TASK 3, SUBTASK 4

DIFFUSION STUDIES

Contract DAAK11-81-C-0101

to

UNITED STATES ARMY
TOXIC AND HAZARDOUS MATERIALS AGENCY

by

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EXECUTIVE SUMMARY

The ability for liquid and gaseous decontaminants to penetrate mortar was investigated in this subtask. Aqueous solutions and FREON® 113 were applied to mortar coupons by spraying and by a constant contact method. The diffusion rate of gaseous NH_3 (a candidate CW agent decontaminant) through mortar was determined.

Experimental results indicate spraying is the preferred method for application of aqueous based decontaminants to concrete. Penetration depths of ¼ to 1 inch were achieved with the spraying method. Operating parameters were determined for further evaluation of the spraying method in subsequent subtasks (5, 6 and 7) of both Task 3 (agents) and Task 4 (explosives).

Gaseous NH_3 has been demonstrated to readily penetrate one inch thick mortar coupons. Further evaluation of the NH_3 decontamination concept will be performed if a replacement concept is required in subsequent subtasks of Task 3.

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TEST REPORT FOR
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to
UNITED STATES ARMY
TOXIC AND HAZARDOUS MATERIALS AGENCY

1.0 INTRODUCTION

In the previous phase [Task 1 (agents) and Task 2 (explosives)], ideas were systematically developed into concepts for decontaminating buildings and equipment. These concepts were evaluated and ranked with respect to technical and economic factors. Because facility decontamination includes decontamination of trace quantities of agents or explosives which have penetrated into porous materials such as concrete, a criterion was incorporated in these evaluations which focused on the anticipated depth of penetration of the decontaminant into porous materials. It was assumed that the depth of penetration of chemical decontaminants would be less than 1/8 inch for liquids and more than 1/8 inch (but less than complete penetration) for gases. It was recognized that an experimental effort would be required to substantiate these penetration depths. Furthermore, knowledge gaps relating to the application of the decontaminant on to concrete (e.g., application rates, application times and equipment selection) were identified for experimental evaluation.

2.0 OBJECTIVE/SCOPE OF STUDY

The objectives of this subtask were to determine

- the feasibility of application of liquid decontaminants to concrete by spraying;

- the liquid and recycle requirements, application times, and preliminary equipment requirements for a subsequent engineering/economic analysis;
- the feasibility of a sustained application method for liquids such as the use of gels or foams;
- exposure times for the application of NH_3 gas to agent-contaminated concrete structures;

The potential decontaminants investigated in this subtask included:

- Aqueous solutions - with and without surfactants or co-solvents
- Monoethanolamine (MEA) - aqueous solution
- Gaseous NH_3 (anhydrous)
- FREON 113 solvent

Since these decontaminants/solvents are representative of the chemical and physical decontamination fluids to be used for both agents and explosives, the results of this subtask will be utilized in both Task 3 (aqueous solutions, MEA, NH_3, and FREON 113) and Task 4* (aqueous solutions and FREON 113).

The three application methods investigated included:

- Spraying
- Constant contact
- Gaseous diffusion

3.0 TEST COUPONS

3.1 Description

Concrete is composed of mortar (sand, cement, and water) and aggregates. In this subtask, 5 inch by 5 inch square by 1/4, 1/2 or 1 inch thick mortar coupons (no aggregate) were used for all experiments. Aggregates were not added to the mortar mix because typical aggregates used in commercial

* A related effort focusing on decontamination cf explosives.

concrete preparations were too large to be used in the coupons. The maximum size of suitable aggregate is determined by taking one-third the size of the smallest dimension of the mold. Because one-fourth inch thick coupons were used in most of the tests, the largest aggregate should be no larger than one-twelfth inch in size (equivalent to sand). Typical commercial aggregate is a minimum of one-fourth inch in size. Also, a material such as basaltic aggregate (typically used as aggregate portion of concrete) has a low permeability and a low porosity. As such, there are relatively few pores into which liquids or gases (i.e., water, decontaminants, agents, explosives, etc.) can penetrate. Limestone, another typical aggregate, is relatively permeable as compared with basalt but has a permeability comparable to mortar.

High porosity and low porosity mortar coupons were prepared for use in all tests. The literature search, states that the water-to-cement ratio (W/C) has the greatest effect on the porosity of the mortar (see Appendix A). As such, the mortar test coupons were cast using two different water-to-cement ratios in order to achieve the two different porosities. The amount of sand added for each type was determined from the preparation of trial batches described in Appendix B.

Most of the cast coupons were allowed to cure for at least 14 days* in a room maintained at 100 percent relative humidity. The coupons were then allowed to equilibrate to ambient humidity (see Appendix B). A slightly longer cure time is usually recommended to increase the long-term strength and durability of mortar. However, the porosity of mortar does not markedly change after a 7-day cure and it was found that nearly all of the 14-day cured coupons were durable enough to withstand testing.

3.2 Coupon Porosities

A breakdown of the average, highest, and lowest porosities, are included in Table 1 for each type of coupon cast. As shown in Table 1, the low porosity, 1/4-inch thick coupons that were cured for 14 days had an

* Ten low porosity coupons were allowed to cure for only 7 days in order to initiate the spray experiments sooner.

average porosity of 11.6 percent; the highest being 11.7 percent, and the lowest, 11.5 percent. This variation in porosity was considered small enough that the porosity of every low porosity, 1/4-inch thick coupon cured for 14 days was not experimentally determined. However, a large variation in the porosity for the other coupons was observed, thereby requiring that a porosity determination be made on each coupon used in a test. The experimental technique used to determine porosity is described in Appendix C.

TABLE 1. COUPON POROSITIES

Cure Time (days)	Water:Cement ratio*	Thickness (in)	Lowest porosity (vol %)	Average porosity (vol %)	Highest porosity (vol %)
7	0.4	¼	12.7	13.1	13.5
14	0.4	¼	11.5	11.6	11.7
14	0.6	¼	15.3	17.0	18.6
14	0.4	½	9.7	11.5	13.0
14	0.6	½	10.5	13.6	15.9
14	0.4	1	6.8	7.3	8.3
14	0.6	1	11.4	12.2	13.2

* In this report, all coupons prepared with a 0.4 water / cement ratio are referred as low porosity coupons. All coupons prepared with a 0.6 water / cement ratio are referred as high porosity coupons.

4.0 SPRAYING EXPERIMENTS

The spraying experiments identified trends in conditions for the application of aqueous solutions and FREON® to mortar by spray application. The spraying variables which were experimentally evaluated included:

- Nozzle type
- Supply pressure

- Coverage
- Interval

For each variable, two or three conditions were selected such that the effect of the variable (i.e., trends) on the penetration rate of liquid into mortar could be determined. The range of values selected for each variable and the rational for their selection are given in Table 2. In addition to these spraying variables, solution and mortar properties were varied. The solutions and mortar types which were experimentally evaluated included:

Solutions

- Water
- Water/Solvent
  - -5 percent acetone/water**
  - -50 percent acetone/water**
  - -10 percent DMSO/water**
  - -40 percent DMSO/water**
- Water/Surfactant
  - -0.1 percent Triton X-100
  - -1.0 percent Triton® X100
- 50 percent MEA/water
- FREON® 113

Mortars

- 1/4-inch thick low and high porosity
- 1/2-inch thick low and high porosity
- 1-inch thick low and high porosity

Because of the large number of experiments required to evaluate all possible combination of variables,* the number of experiments were reduced. The logic used to reduce the number of experiments is shown in Figure 1.

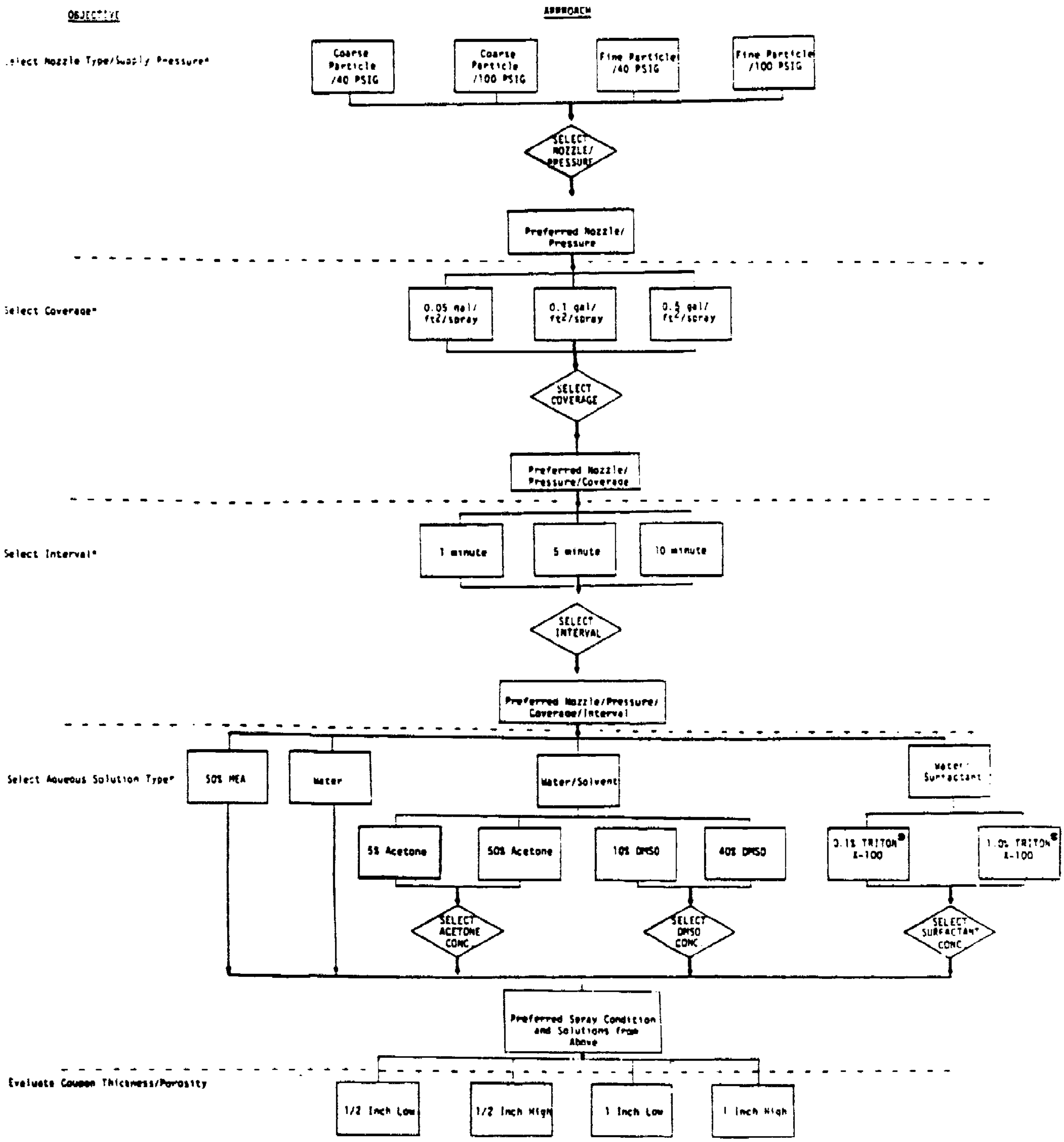
---

* Two nozzle types x 2 pressures x 3 coverages x 3 intervals x 9 solutions x 6 mortars - 1944 experiments

** Investigated as a solvent for either explosives or C.W. agents.

TABLE 2. SELECTED VALUES FOR SPRAYING VARIABLES AND RATIONALE FOR THEIR SELECTION

Test Variable	Selected Valves	Reason for Selection of Valves
Pressure	40 and 100 psig	Typical operating pressures for many commercial spraying units. Sufficiently different pressures such that the effect of pressure on liquid penetration can be determined. Higher pressures (e.g., 400 psig) were not selected because abrasion of the mortar would occur. Abrasion would cause building damage and the need to process solid residue, both of which are not desirable.
Nozzle type	Fine particle (100-300μ) and coarse particle (500-1000μ)	Sufficiently different particle sizes such that the effect of particle size on liquid penetration can be determined. Trends in the data will determine whether or not smaller particles (less than 100μ) would be preferred. Smaller particles would require the use of nebulizers or atomizers and affect the physical removal/decontamination process. Commercial spray nozzles which emit longer particle sizes are available. However, these nozzles require much larger flow rates (e.g., 10 to 30 gpm) which are not desirable because of (1) large material requirements and (2) the need to process large quantities of waste solution for recycle and disposal.
Coverage	0.05, 0.1 and 0.5 gal/ft^2/spray	Sufficiently different coverages such that the effect of coverage on liquid penetration can be determined. Higher coverages (e.g., greater than 1.0 gal/ft^2/spray) are not desirable because of large material/recycle requirements. Trends in the data will determine whether or not lower coverages would be preferred.
Interval	1, 5, and 10 minute	Sufficiently different intervals such that the effect of internal on liquid penetration into mortar/evaporation from the mortar surface can be determined. Trends in the data would suggest the time required for the film on the mortar surface to be depleted by adsorption into the mortar/evaporation from the mortar.



* Both 1/2-inch low porosity and high porosity coupons were used in the tests.

FIGURE 1 METHOD OF SELECTION OF PREFERRED PARAMETERS IN SPRAYING EXPERIMENTS

4.1 Description of Spraying Experiments

4.1.1 Spraying Apparatus

The spraying apparatus, shown in Figure 2, consisted of a pressure vessel, a hose, a spray gun, spray nozzles and a shield assembly. A pressure vessel was used to supply pressurized liquid at 40 psig and 100 psig. The liquid, at room temperature, was sprayed on the coupons which were installed in the shield shown in Figures 2 and 3. The spray gun was calibrated at various operating pressures to deliver specified flow rates.

The 5-inch square test coupon was clamped behind a 4-inch square opening in a framed shield. The shield was supported in such a way that the face of the test coupon was vertical as shown in Figure 2. This shield served as a support for the coupon and insured that only the surface of the coupon was exposed to the decontaminant spray solution or solvent. The spray shield was modified from that described in the test plan by adding three 1 ft x 2 ft x 1/4" pieces of PLEXIGLAS® perpendicular to the front face of the shield to contain the overspray.

A rubber gasket was placed around the perimeter of the opening, between the spray shield and the coupon, to prevent moisture from seeping around the coupon. The test coupon, shield, and support were placed in a basin to collect all the run-off decontaminant solution or solvent.

4.1.2 Test Variables/Data

The following is a list of parameters identified for each spraying experiment:

- Original Weight (W_0) - weight of coupon equilibriated to ambient humidity (grams)
- Weight Change (W_i) - difference between the weight of a coupon after a number of intervals, and the original weight of the coupon (grams)

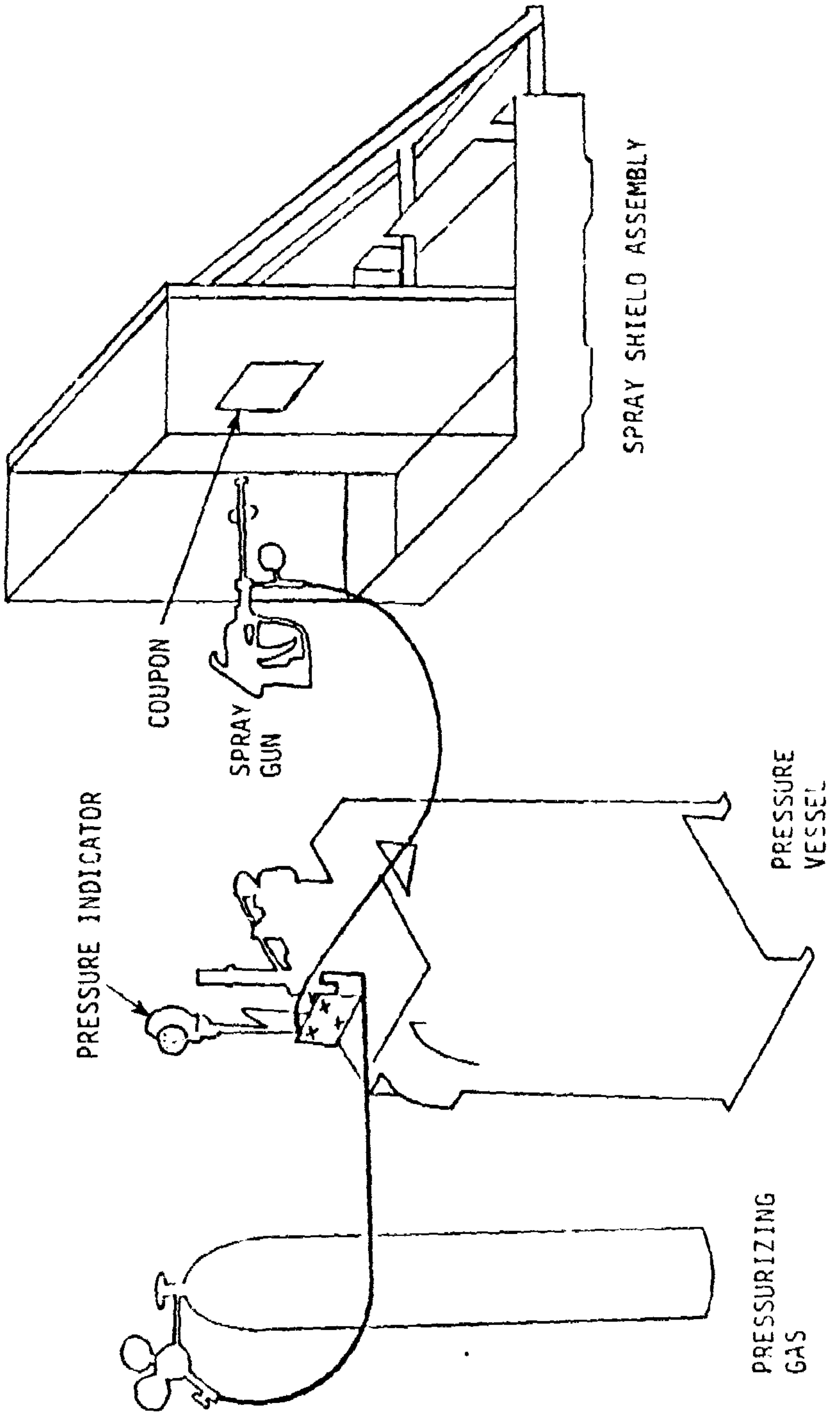


FIGURE 2. SPRAYING APPARATUS

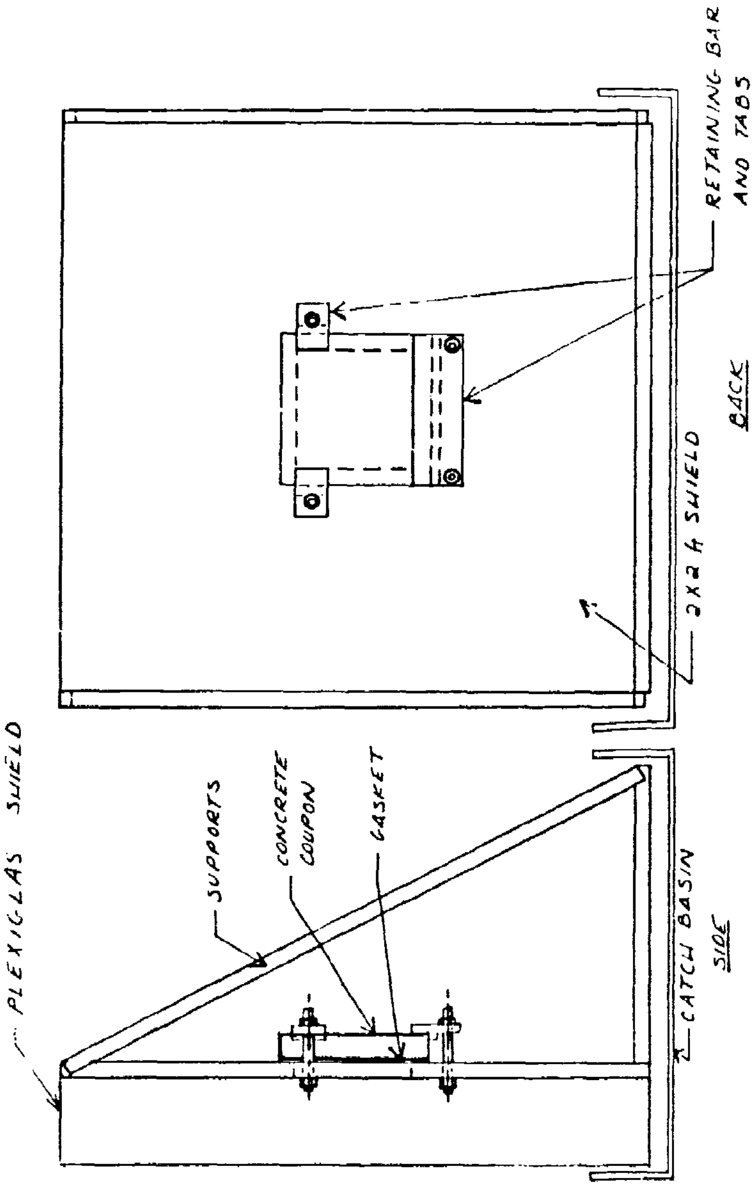


FIGURE 3. SPRAY SHIELD ASSEMBLY

- Interval - corresponds to one spray cycle
- Weight of Saturated Coupon (W_{SAT}) - Weight of coupon completely saturated with water (grams)
- ΔW = Dimensionless coupon weight gain = $W_t/(W_{SAT} - W_0)$ = coupon weight gain by absorption of liquid divided by weight of liquid absorbed by a saturated coupon.
- Interval Time (T_i) - the time between the start of each spraying (min) = sum of spray time and idle time
- Spray Time (T) - the time required to spray a given amount of liquid on the surface of the coupon during one interval (min)
- Total Spray Time (ΔT) - the summation of the spray times over given number of intervals (min)
- Idle Time - the time the coupon was not subjected to a spray within a given interval (min)
- Total Idle Time - the summation of the idle time over a given number of intervals (min)
- Coverage - the amount of liquid sprayed in each interval per unit area covered (gal/ft^2 of coupon area/spray)
- Pressure - liquid supply pressure
- Nozzle Type - based on the average particle size of the spray (Nozzle manufacturer's data)
- Porosity - relative measure of the void space available in the coupon

The relationships between spray time, idle time, and the spray cycle interval are illustrated in Figure 4.

4.1.3 Test Procedure

The following procedure was used in conducting the spraying experiments:

1. Select and record nozzle, pressure, coverage, interval, and solution.

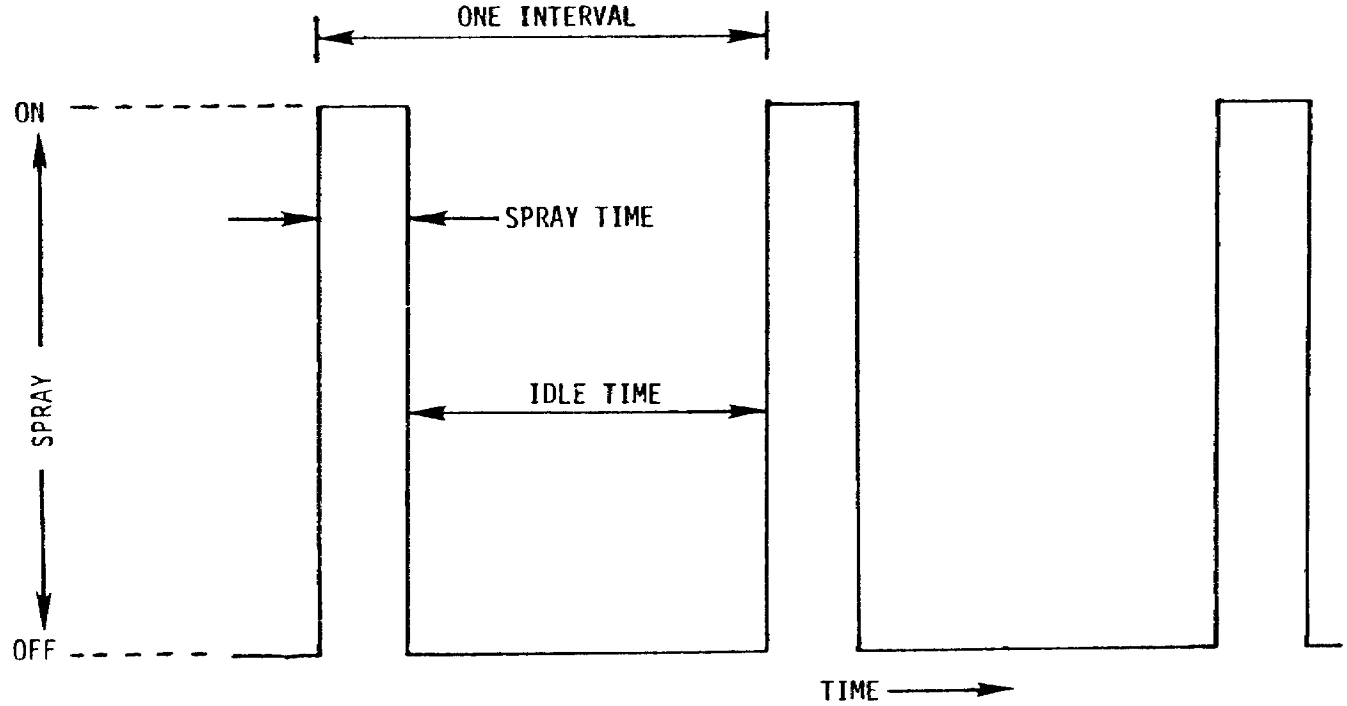


FIGURE 4. RELATIONSHIP BETWEEN SPRAY, IDLE, AND INTERVAL TIME

2. Calculate spray time.
3. Record starting time, temperature, relative humidity, initial amount of solution charged in pressure vessel, coupon number, coupon thickness (1/4, 1/2 or 1 inch) porosity of coupon (high or low), and initial weight of coupon.
4. Install coupon in shield.
5. Start clock and spray for calculated spray time
6. Record time first interval began.
7. Repeat spraying for the calculated spray time at the beginning of each interval.
8. After every fifth interval (beginning of sixth interval), wipe coupon with a damp cloth and remove from the shield.
9. Weigh coupon on a balance accurate to ± 0.01 grams
10. Record time, weight, weight change, and if penetration had occurred.
11. Re-install coupon in shield, spray, and record time and interval.
12. Repeat steps 7 through 11 until either the fortieth interval is reached for 1/4-inch coupons or the eightieth interval for 1/2-inch and 1-inch coupons.
13. Save coupon for porosity determination (as required).
14. Add liquid to pressure vessel when needed.
15. Collect and record amount of run-off liquid from spray shield.
16. Determine final amount of liquid in pressure vessel.

Several steps of the procedure are further described below.

4.1.3.1 Spray Time Calculation. Prior to performing the experiments, the flow rate from each nozzle was calibrated by measuring the delivery rate of liquid from the nozzle for a 40 and a 100 psig supply pressure. Once

the flow rate was calibrated, the time the spray must be maintained for each spraying (spray time) was calculated as follows:

$$\text{Spray Time (min)} = \frac{\text{Coverage (gal/ft}^2\text{) x Coupon Area (ft}^2\text{)}}{\text{Flow Rate (gal/min)}}$$

4.1.3.2 Coupon Wiping/Weighing. Before weighing, the coupon was wiped with a damp towel to keep the liquid from seeping around to the back of the coupon. Wiping removed water drops and the thin film of liquid from the surface of the coupon. The weight recorded was the weight of the coupon and the liquid that had permeated into the coupon. Because the weight did not include the weight of the residual surface drops and film, a more representative weight gain due to fluid penetration was obtained. The method of wiping with a damp towel is recommended by ASTM Method C-20.

For most of the tests, the weight change was measured every fifth interval rather than every interval.

4.1.3.3 Nozzle Distance. The distance the nozzle was held from the coupon was unique to each nozzle and supply pressure. The distance was determined by holding the nozzle at the farthest distance from the coupon such that the largest dimension of the spray pattern would spread 4 inches (the surface to be sprayed was 4 inches square). Care was taken to assure that the coupon was sprayed uniformly and that all spray impinged on the coupon.

4.1.3.4 Number of Intervals. The 1/4-inch thick coupons were sprayed for 40 intervals before each experiment was terminated. The majority of the 1/4-inch coupons reached an approximate constant weight gain ($\pm$ 0.1 g/spray) after 35 intervals.

The 1/2-inch and 1-inch coupons were sprayed for 80 intervals before each experiment was terminated. Although fluid penetration through the back of the coupon was not observed after spraying some of the 1/2-inch and most of 1-inch coupons after 80 intervals, a comparison between experiments was still possible.

4.1.3.5 Penetration Time. The time for penetration of liquid through the coupon was determined by noting a wet spot on the back of the coupon (usually near the center of the coupon) away from any areas potentially wetted by seepage around the coupon (usually only observed near the bottom of the coupon).

4.1.3.6 Material Balances. Attempts were made to perform material balances by a comparison of amount of liquid applied with that recovered during each experiment. That which could not be accounted for was attributed to the following reasons. The first was due to absorption of liquid into the concrete coupon which accounts for approximately 1 percent of all losses. The second was from unrecoverable residual liquid in the catch basin, liquid droplets on the shield, and errors in volume measurement which accounted for approximately 10 percent of all losses. The other losses were overspray and evaporation with overspray accounting for the majority of liquid loss. Because of the losses, the total amount of liquid applied during an experiment was measured as the difference between the initial and final amount of liquid in the pressure vessel. In some experiments, the liquid supply in the pressure vessel was depleted before the end of the experiment. In such cases, the pressure vessel was vented to ambient pressure, filled with a measured quantity of liquid, and repressurized.

4.1.3.7 Temperature/Relative Humidity. During the spray experiments and evaporation tests, the relative humidity was found to vary between 30 and 40 percent RH. The room temperature was also continuously monitored and found to vary from 66 to 76 F. The room air velocity was neither measured nor controlled. However, similar laboratory conditions were maintained for all tests (e.g., door to laboratory open at all times, fume hoods on at all times, etc.) such that the air movement velocity at the bench top was nearly the same for all tests.

4.2 Discussion of Spraying Experiments Results

The results of the spraying experiements are discussed in the following sections. Actual data obtained from the experiments identified

in Table 3 are given in Battelle Laboratory Record Books Nos. 39109 and 39265.

4.2.1 Data Analysis Method

During the spraying experiments, the weight change of the coupon and spray time were monitored. The weight change of the coupon, as a result of spraying, is directly related to the degree of penetration of the liquid and is also related to the saturated weight of the coupon. To lessen the effect of a varying saturated weight (due to variations in the porosity of the coupons) and to give a more accurate representation of the data, the weight gain after a given interval (W_i) was divided by the saturated weight (W_{SAT}) minus the original weight (W_o).

Therefore $$\Delta W = \frac{W_i}{(W_{SAT} - W_o)}$$

The weight change (ΔW) was then plotted versus the total spray time ΔT. It is desired to maximize the weight change (ΔW) while minimizing the total spray time (ΔT) since the total spray time is directly proportional to material requirements (amount of liquid applied and amount of liquid requiring recycle/disposal) and operating requirements (manhours). As such, curves with steep slopes (i.e., nearly vertical) represent more optimum application conditions than curves which slope only slightly (i.e. nearly horizontal).

It is important to note that W_{SAT} is the weight of the coupon entirely saturated with water. Since only a 4 by 4 inch section of the 5 by 5 inch coupon was sprayed, a ΔW equal to $(4x4)/(5x5) = 0.64$ represents complete saturation of a 4 by 4 inch section of the coupon. A ΔW greater than 0.64 indicates that the liquid diffused in the direction of the sides of the coupon (i.e., perpendicular to the spray plane).

4.2.2 Selection of Operating Parameters

The following sections discuss results used to select the supply pressure, the nozzle type, the coverage, and the spray cycle interval.

TABLE 3. PARAMETERS VARIED DURING SPRAYING EXPERIMENTS

Experiment Number	Solution Used[a]	Coupon[b] Porosity	Coupon Thickness (inch)	Interval (min)	Coverage (gal/ft²/spray)	Nozzle[c] Type	Pressure (psig)
1	Water	7 day-L	¼	1	0.1	C	40
2						C	100
3						F	40
4						F	100
7					0.5	C	100
8						F	40
9							100
10		L			0.1		100
11					0.1	C	40
16					0.5		
17		H			0.1		
18					0.1		100
19					0.5		40
20							100
21						F	40
22							100
23					0.1		40
24					0.1		100
25		L			0.05	C	40
26		H					40
27		L					100
28		H					100
29		L				F	40
30		H					40
31		L					100
32		H					
33		L		10		C	
34		H		10			
35		L		5			
36		H					
37	1.0% TRITON X-100	L					
38	"	H					
39	0.1% TRITON X-100	L					
40	"	H					
41	40%DMSO[d]	L					
42	"	H					
43	10% DMSO	L					
44	"	H					
45	50% ACETONE	L					
46	"	H					
47	5% ACETONE	L					
48	"	H					
49	50% ACETONE	L	½				
50	"	H					
51	Water	L					
52	"	H					
53	40% DMSO	L					
54		H					
55		L	1				
56		H					
57	Water	L					
58	"	H					
59	50% ACETONE	L					
60	"	H					
61	FREON 113	L	¼				
62		H					
63		H					
64	50%MEA	L					
65		H					
66		L	½				
67		H	½				
68		L	1				
69		H	1				

(a) All solutions are aqueous based except Experiments 61 through 63 where neat FREON 113 was evaluated.

(b) H = High Porosity, L = Low Porosity all 14 day cure except as noted.

(c) C = Coarse Spray, F = Fine Spray

(d) DMSO = Dimethyl Sulfoxide

4.2.2.1 Selection of Supply Pressure and Nozzle Type. The first parameters to be considered were the liquid supply pressure and the nozzle type. It was originally believed that the liquid supply pressure and nozzle type, which affect spray particle size and force of spray, would act interdependently and would have a large effect on the penetration of different decontaminating solutions. After completion of several experiments, these parameters were found to have a much less effect than had been anticipated.

Figure 5, which is a plot of ΔW versus ΔT for Experiments 25, 27, 29, and 31, illustrates the effect of the nozzle type and the liquid supply pressure by comparing experiments that have identical parameters except for nozzle type and liquid supply pressure. The constant parameters for this set of experiments were:

- low porosity coupons
- 1/4-inch thick coupons
- spray solution of water
- one-minute interval
- coverage of 0.05 gal/ft^2/spray = 0.006 gallons/spray*

A similar set of data obtained from Experiments 17, 18, 23, and 24, is given in Figure 6. This data which also illustrates the effect of nozzle type and liquid supply pressure involved a slightly different set of constant parameters (high porosity coupons, 0.1 gal/ft^2/spray coverage).

Based on the data given in Figures 5 and 6, the coarse spray nozzle operating at the high pressure is preferred because the coupons achieved a more rapid weight gain as compared with coupons sprayed with other nozzle type/supply pressure combinations. As a result of the increased rate of weight gain the total spray time is minimized which, in turn, minimizes the total material and operating requirements.

The time the spray is maintained on the coupon surface during one spray cycle (i.e., spray time) is also minimum for the coarse spray/high pressure combination. For example, 0.006 gallons were applied in about one second using the coarse spray/high pressure combination which operated at 0.242 gpm. The same amount of liquid was applied in about 3 seconds using the coarse spray low pressure combination which operated at 0.113 gpm.**

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* 0.05 gal/ft^2/spray x (4x4/144) ft^2 = 0.006 gallons/spray.

** (0.006 gallons/0.113 gpm) x 60 = 3 seconds.

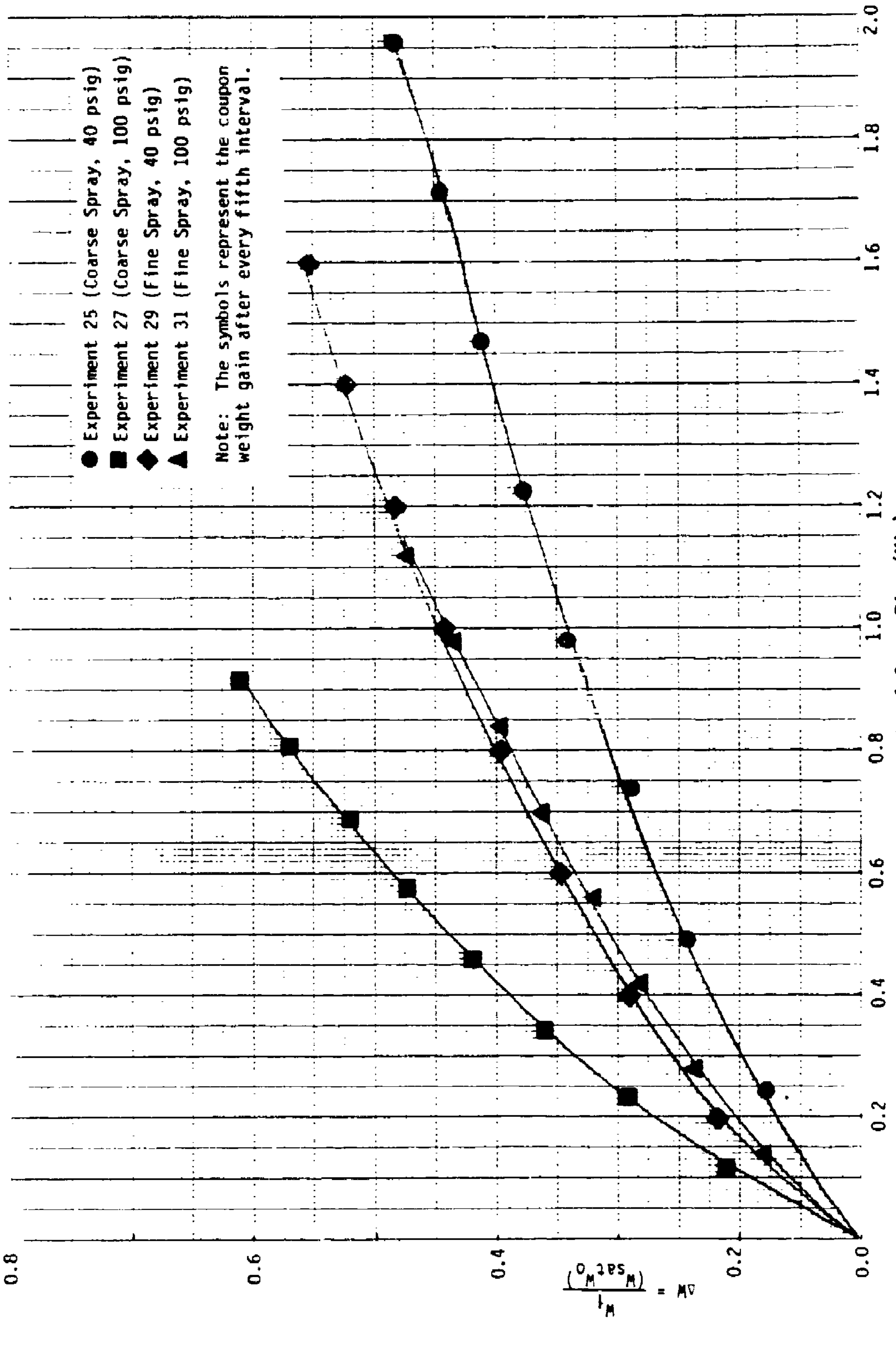

FIGURE 5. EVALUATION OF NOZZLE SPRAY TYPES AND SUPPLY PRESSURE (low porosity coupons)

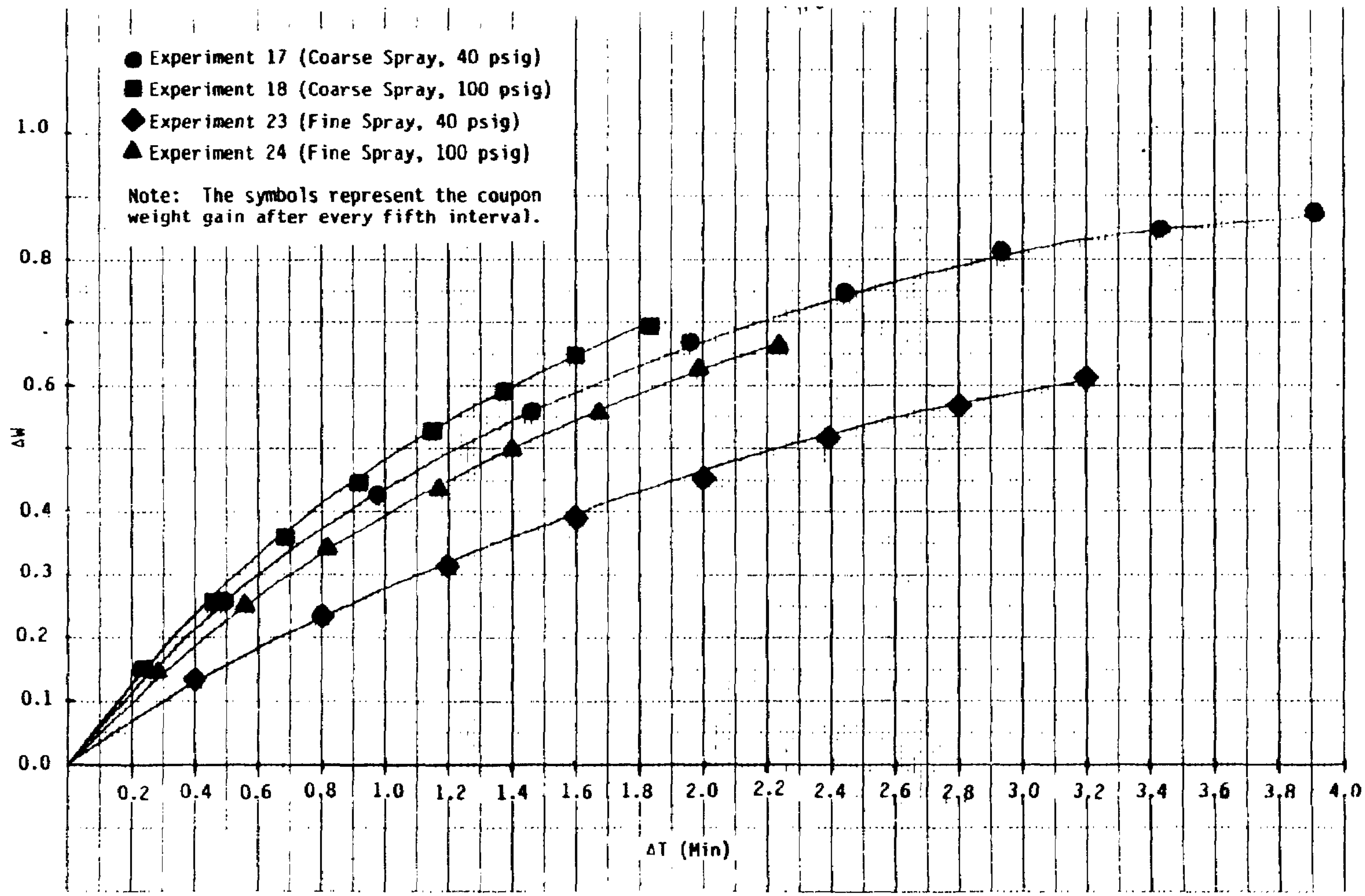

FIGURE 6. EVALUATION OF SPRAY NOZZLE TYPE AND SUPPLY PRESSURE (high porosity coupons)

Because of spray time, the total spray cycle interval and the total liquid applied are minimized, the coarse nozzle and high pressure were selected as preferred operating paramters. A coarse spray nozzle and 100 psig supply pressure were used for all subsequent experiments.

It is also important to note that upon comparison of Figure 5 with Figure 6, the same general trends are apparent irregardless of the porosity of the coupon.

4.2.2.2 Selection of Coverage. A coverage is a measure of the amount of liquid applied to a specific area during one spraying. Coverages of 0.05 and 0.1 and 0.5 gal/ft^2/spray were evaluated. Figure 7 illustrates the effect of coverage by plotting experiments that have identical parameters except for the coverage. The constant parameters for this set of experiments were:

- low porosity coupons
- 1/4-inch thick coupons
- spray solution of water
- one-minute interval
- low pressure
- coarse nozzle

The results given in Figure 8, also illustrate the effect of coverage using a slightly different set of constant parameters (high porosity coupons, high pressure).

From Figures 7 and 8, the lowest coverage of 0.05 gal/ft^2/spray appears to be far better than the highest coverage of 0.5 gal/ft^2/spray but only marginally better than a coverage of 0.1 gal/ft^2/spray. These results indicate that a lower coverage gives the best results and also reflect the fact that there is a limit below which a reduction of coverage would not enhance penetration. The lower limit is probably dependent upon the evaporation rate of the liquid from the coupon.

4.2.2.3 Selection of Spray Cycle Interval. When selecting the spray cycle interval, the mechanism of liquid penetration into mortar must be

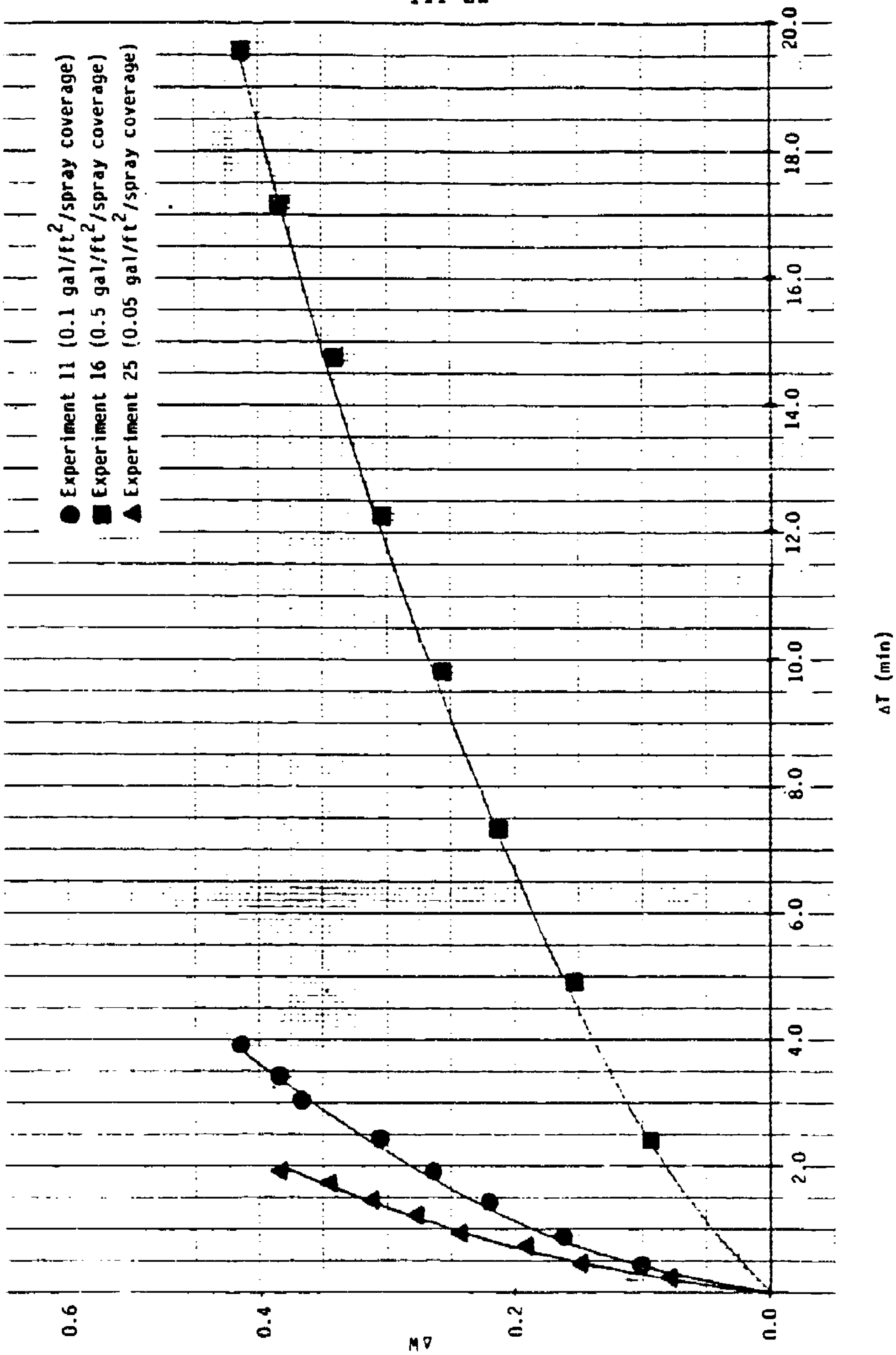

FIGURE 7. EVALUATION OF COVERAGES (low porosity coupons)

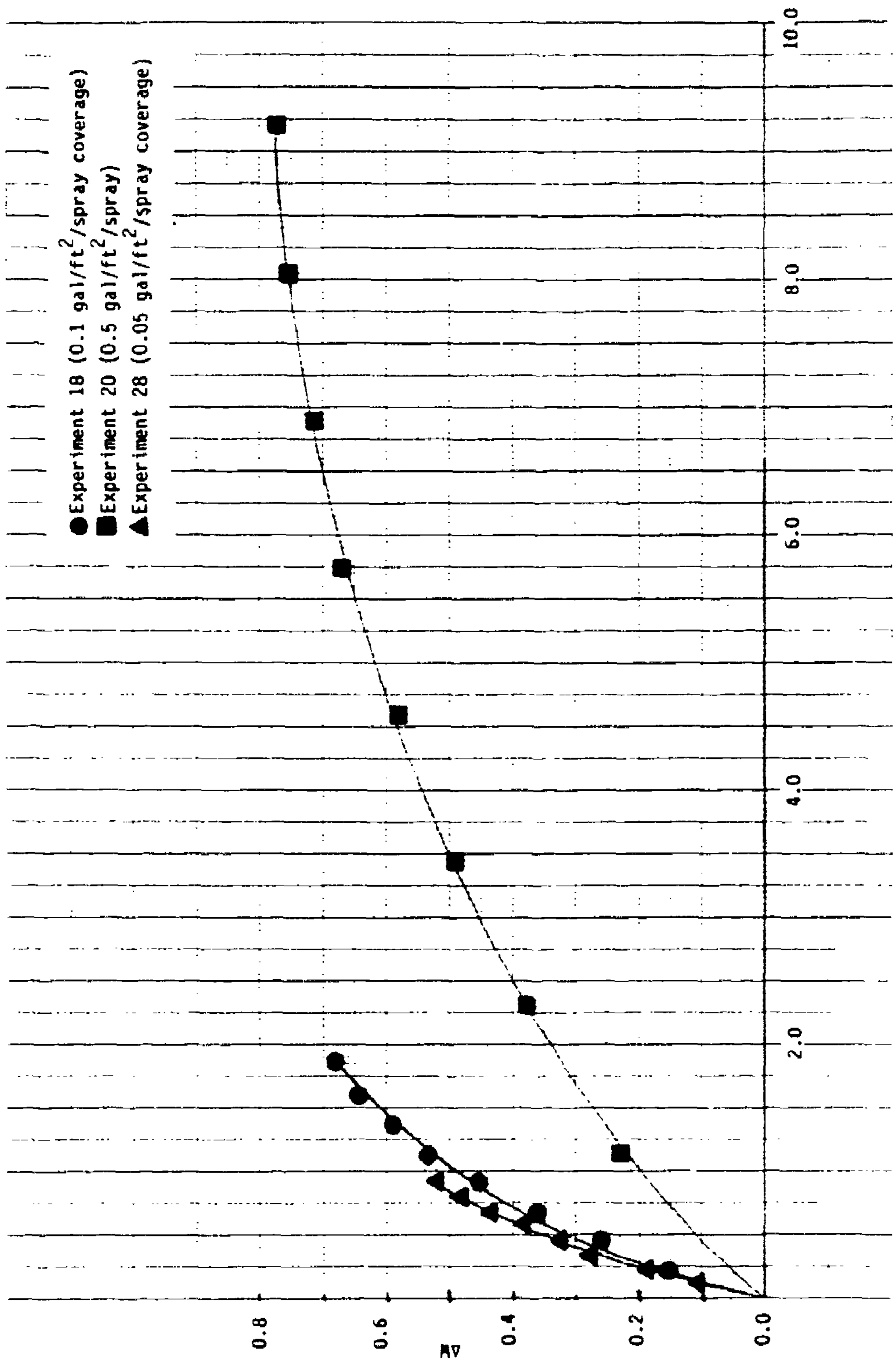

FIGURE 8. EVALUATION OF COVERAGES (high porosity coupons)

considered. The penetration of a sprayed liquid into the mortar coupons occurs during two different periods. The first and most obvious is while the coupon is being sprayed. While the spray is impinging upon the coupon, the surface of the coupon is completely saturated with liquid which can then penetrate into the coupon. The second penetration period occurs between sprayings. During this period (referred to as idle time), a liquid film is still present on the surface, so the penetration of the liquid into the mortar continues. Penetration of the liquid can continue until the film is either completely absorbed and/or evaporated.

At the end of spray-cycle intervals of one minute, the surface liquid film is still relatively thick. Spraying over this film does not enhance penetration and is a waste of material and manpower. At the end of 10-minute spray cycle intervals, the surface liquid film has been completely absorbed and/or evaporated. Consequently, the preferred interval would be one in which the next spray cycle interval starts as soon as the surface film disappears. Based on these observations, the most desirable interval would be somewhere between a one-minute and ten-minute interval.

The results given in Figures 9 and 10 support the above argument by isolating the effects of interval duration (i.e., all parameters constant except in the spray cycle interval). Figure 9 is a plot of Experiments 27, 33, and 35 where the following parameters were held constant:

- 1/4-inch thick coupon
- low porosity coupon
- water solution
- 0.05 gal/ft^2/spray coverage
- coarse nozzle
- 100 psig liquid supply pressure

The results given in Figure 10, are for Experiments 28, 34, and 36, where the same parameters listed above were used except that high porosity coupons were tested. In both Figures 9 and 10, the five-minute interval was shown to be better than either the one-minute or ten-minute interval. As such, a 5 minute interval was used for subsequent experiments. However, it is important to note that the optimum interval is believed to be unique to the type of solution and the porous medium (e.g shorter intervals may be required for volatile solutions).

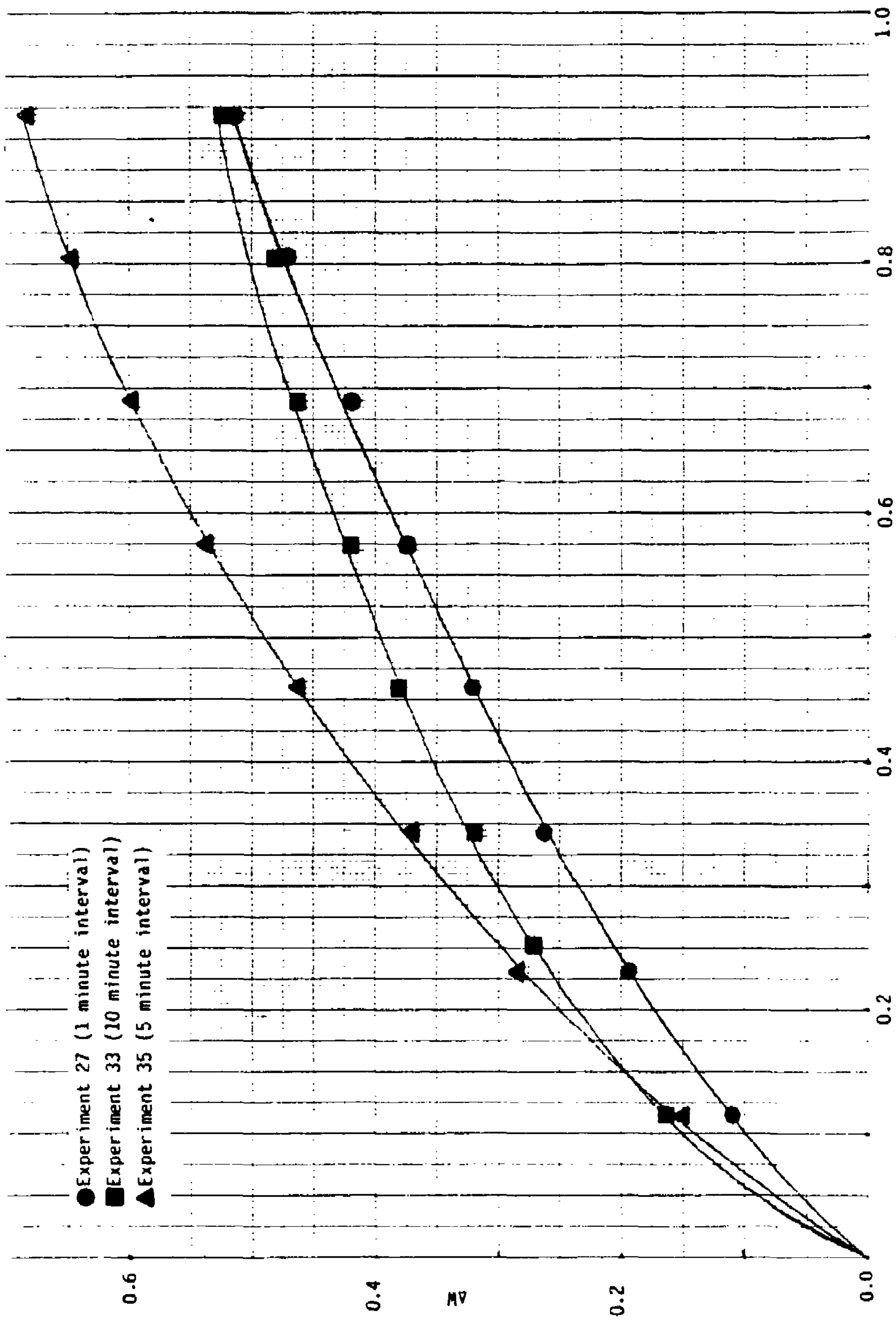

FIGURE 9. EVALUATION OF INTERVALS (low porosity coupons)

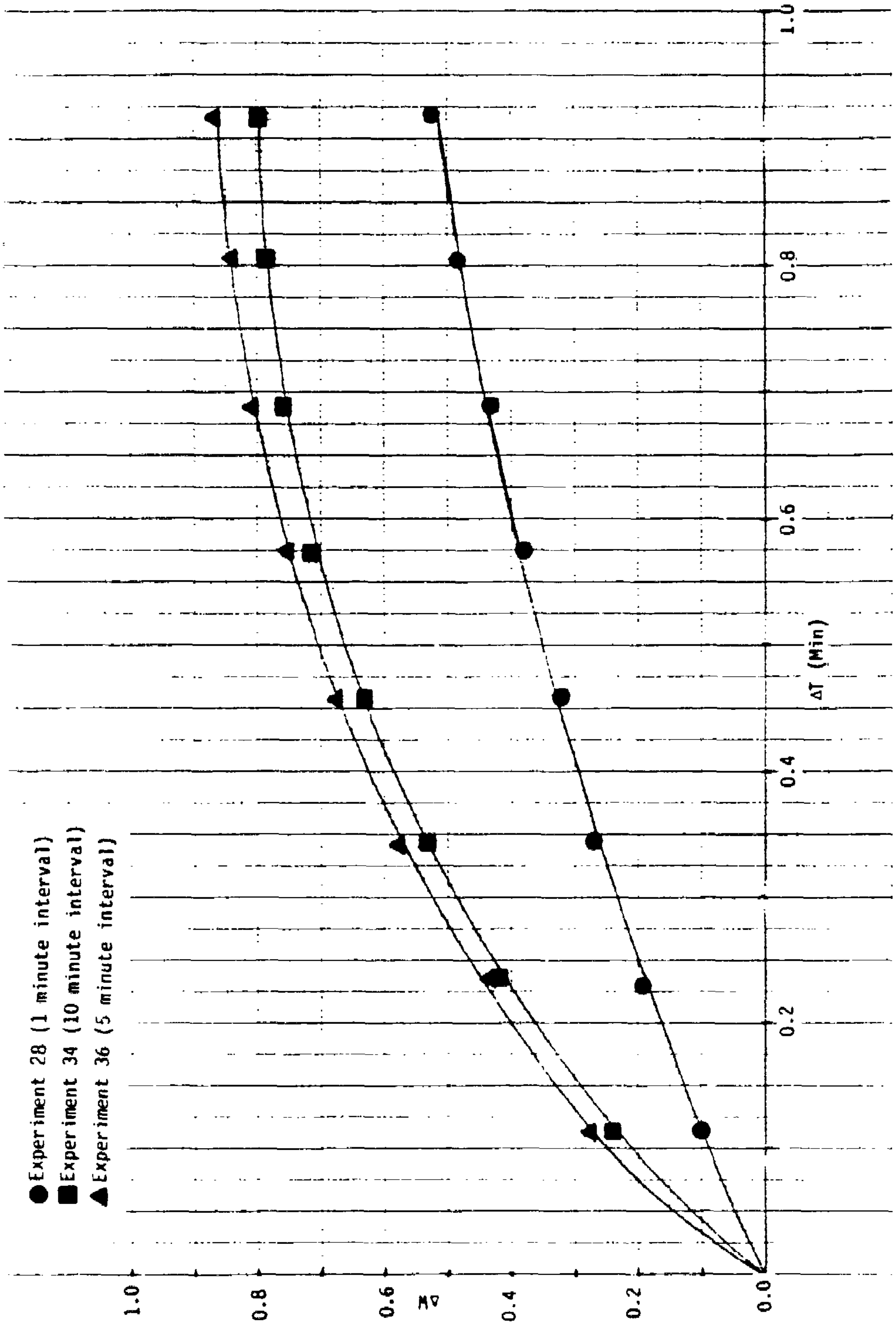

FIGURE 10. EVALUATION OF INTERVALS (high porosity coupons)

<u>4.2.2.4 Summary of Preferred Operating Parameters</u>. The preferred operating parameters for water-like fluids appear to be:

Nozzle Type	-	Coarse spray
Supply Pressure	-	100 psig (6.8 atm)
Coverage	-	0.05 gal/ft^2/spray (2.0 $liter/m^2$/spray)
Interval	-	~ 5 minutes

With all the operating parameters selected, the different water-based decontamination solutions were tested using these parameters.

4.2.3 Selection of Most Effective Aqueous Solutions

Seven different aqueous solutions from three groups (water alone, water-solvent system and water-surfactant system) were experimentally evaluated for their ability to penetrate concrete. The most promising of these solutions were then selected. The seven candidate aqueous solutions were:

- Water
- Water-solvent system - 5 percent acetone in water
  - 50 percent acetone in water
  - 10 percent DMSO* in water
  - 40 percent DMSO in water
- Water-surfactant system - 0.1 percent Triton X-100** non-ionic surfactant in water
  - 1.0 percent Triton X-100 non-ionic surfactant in water

Results of these spraying experiments are shown in Figures 11 and 12.

Figure 11 illustrates experiments which evaluated the aqueous solutions using the best operating parameters described in Section 4.2.2.4 and 1/4-inch low porosity coupons. The results indicate that the Triton X-100 solutions gave the poorest penetration and that the three best aqueous solutions were water, 5 percent acetone and 10 percent DMSO. These were

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* Dimethyl Sulfoxide

** Alkyl Phenoxy polyethoxy ethanol.

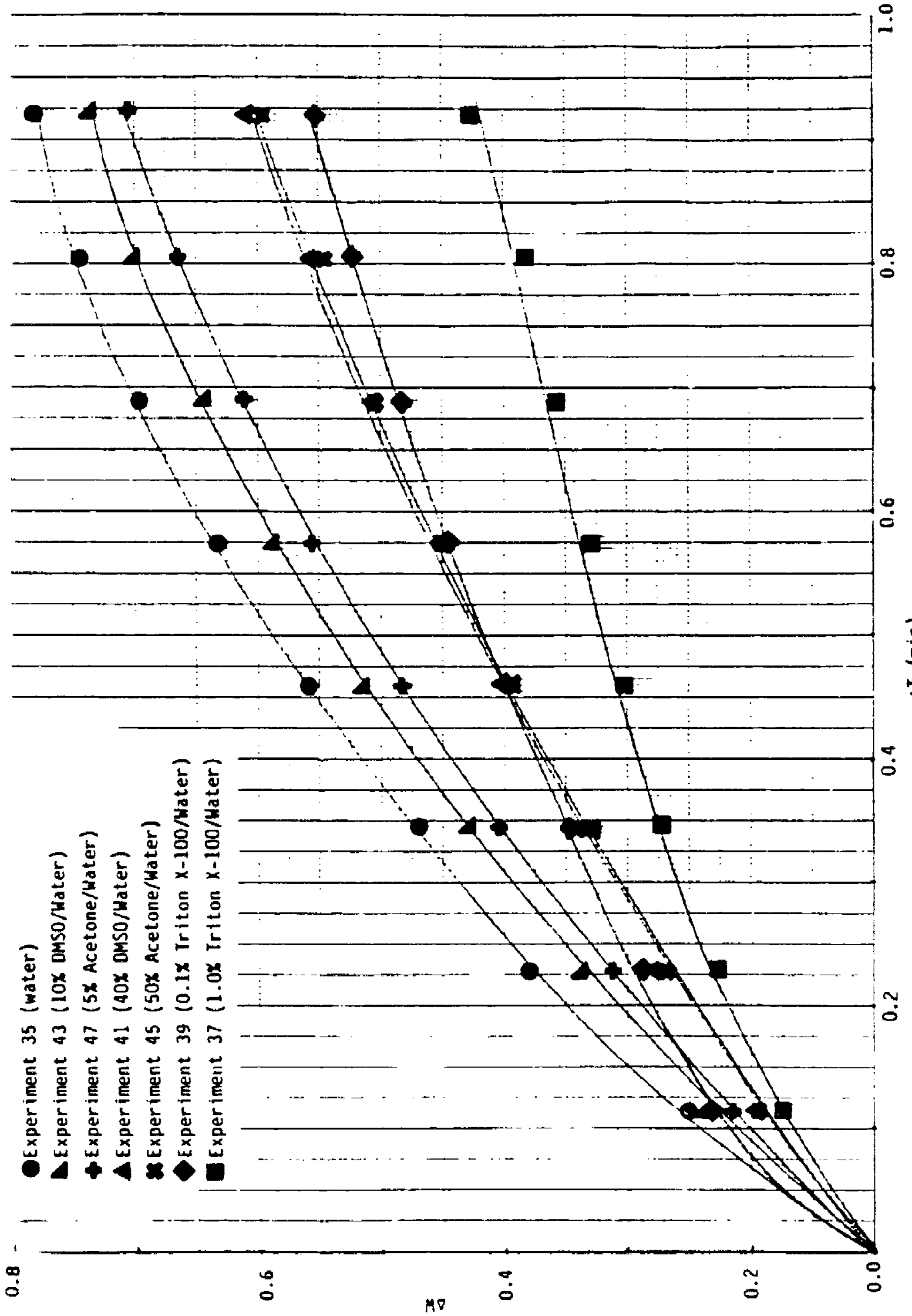

FIGURE 11. EVALUATION OF AQUEOUS SOLUTIONS (low porosity coupons)

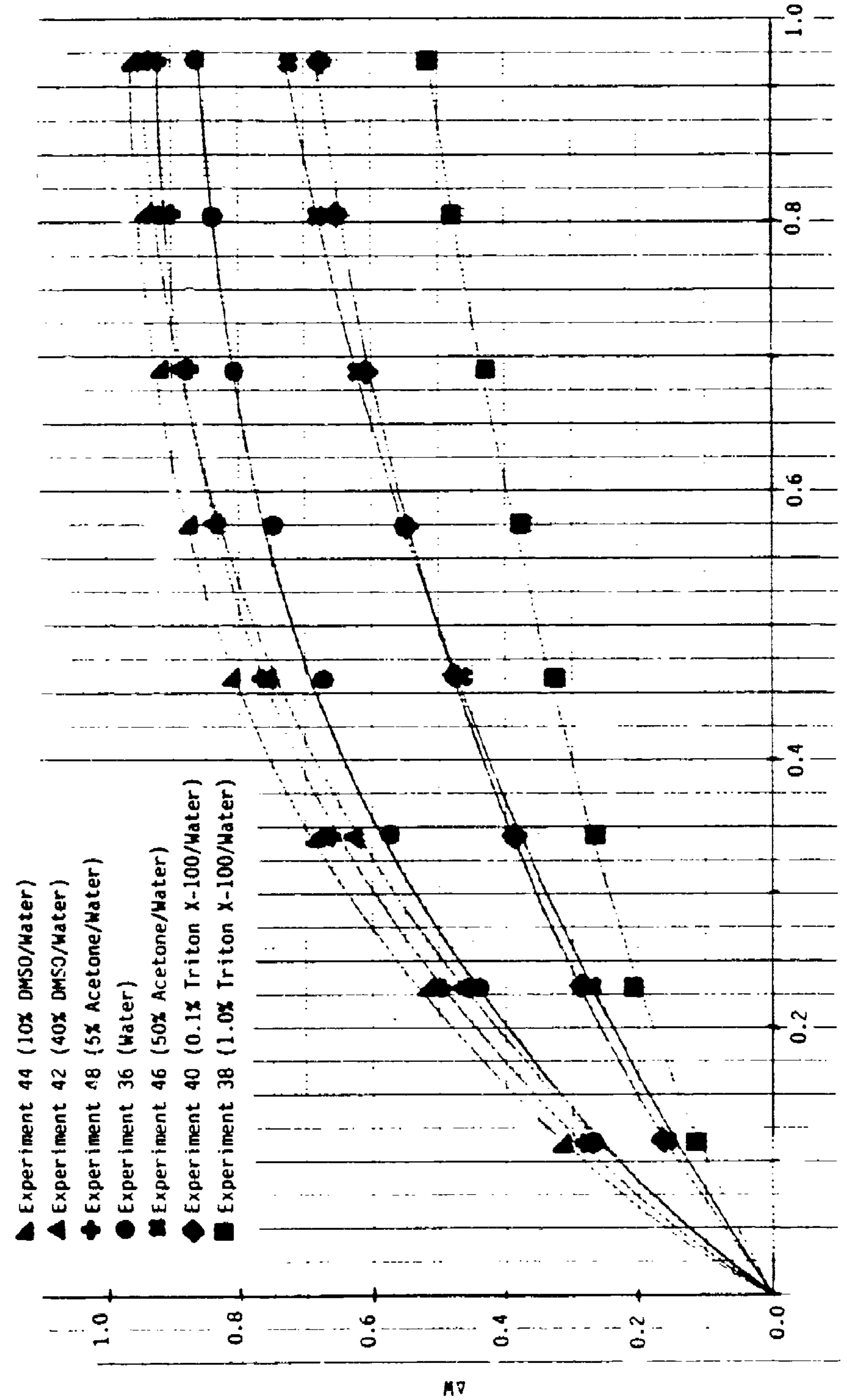

FIGURE 12. EVALUATION OF AQUEOUS SOLUTIONS (high porosity coupons)

followed by 50 percent acetone and 40 percent DMSO. Figure 12 illustrates experiments identical to the ones given in Figure 11, except high porosity coupons were used. In this case the best results for high porosity coupons were achieved with 10 percent DMSO followed by 5 percent acetone, 40 percent DMSO, water, and 50 percent acetone, respectively. Considering the results in both Figures 11 and 12, the three solutions that gave the best penetration results were water, 5 percent acetone, and 10 percent DMSO. The rankings of all solutions are shown in Table 4 along with their corresponding surface tension and viscosities. An interesting trend shown in Table 4 is the effect of surface tension on the rate of penetration of liquid into mortar. It appears that the higher the surface tension, the higher the rate and degree of penetration. As such, aqueous solutions with high surface tensions are favored over aqueous solutions containing additives which lower surface tension (i.e., organic solvents or surfactants). In contrast to the effect of surface tension on penetration rate, a similar relationship to viscosity was not observed.

A factor which must be considered before the most effective solutions can be selected is their ultimate use. Task 4, Subtask 3 efforts* have focused on solubilizing explosives with aqueous solutions (i.e., water/surfactant, water/DMSO, water/acetone). Results from these efforts indicate 1) surfactants do not markedly affect the solubility (rate and degree) and 2) organic co-solvents such as DMSO or acetone increase the solubility if present in water in relatively high concentrations (about 50 percent). Thus, because surfactants neither increased the penetration rate into mortar nor caused a marked increase in the solubility of explosives; aqueous solution containing surfactants were eliminated from further consideration. Because low concentrations of organic co-solvents do not markedly increase the solubility of explosives in water, the 10 percent DMSO and 5 percent acetone aqueous solutions were eliminated from further consideration. Although the penetration rate into mortar is compromised, high concentrations of DMSO or acetone in water are required for improved explosive solubility. Further

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* A related program focusing on explosive decontamination.

TABLE 4. RANKING OF AQUEOUS SOLUTION PENETRATION RATES AS COMPARED WITH THEIR SURFACE TENSION AND VISCOSITY

Symbol (From Fig. 11 & 12)	Rank	Solution	Surface Tension (dynes/cm)[a]	Viscosity (centipoise)[a]
●	1	Water	72	1.0
◣	2	10% DMSO	66	1.25
✚	3	5% Acetone	56	1.1
▲	4	40% DMSO	55	2.30
✖	5	50% Acetone	30	1.4
◆	6	0.1% Triton X-100	30	1.01
■	7	1.0% Triton X-100	30	2.5

(a) Data Source: Manufacturers data sheets and CRC Handbook of Chemistry and Physics, 53rd Edition, 1972. Reference temperatures are between 20 and 25C.

testing of solutions related to explosive decontamination was limited to the following aqueous solutions:

- Water
- 50 percent acetone/water
- 40 percent DMSO/water

4.2.4 Effect of Coupon Thickness on Penetration Rates

Three coupon thicknesses (¼, ½ and 1 inch) were used to investigate the effect of coupon thickness on penetration rates. The following solutions were evaluated:

- Aqueous Solutions - water alone
  - 50 percent acetone/water
  - 40 percent DMSO/water
- FREON 113
- 50 percent MEA in water*

4.2.4.1 Aqueous Solutions. The results from experiments using water are given in Figure 13. The effect of coupon thickness on penetration rate was determined in these experiments by using the best operating parameters, all three coupon thicknesses, 40 percent DMSO/water experiments and the 50 percent aceton/water experiments in Figures 14 and 15, respectively.

If all three figures are considered simultaneously, it is obvious that the rate of penetration is the fastest for the 1/4-inch coupons followed by 1/2-inch, then 1-inch coupons. In general, the rate of penetration is also more rapid for high porosity coupons than for low porosity coupons of the same thickness.

A possible explanation for the effect of coupon thickness on the penetration rate is as follows. As the thickness of a porous material increases, the path through which a fluid travels from one side of the

* MEA = Monoethanolamine - a candidate CW agent decontamination solution.

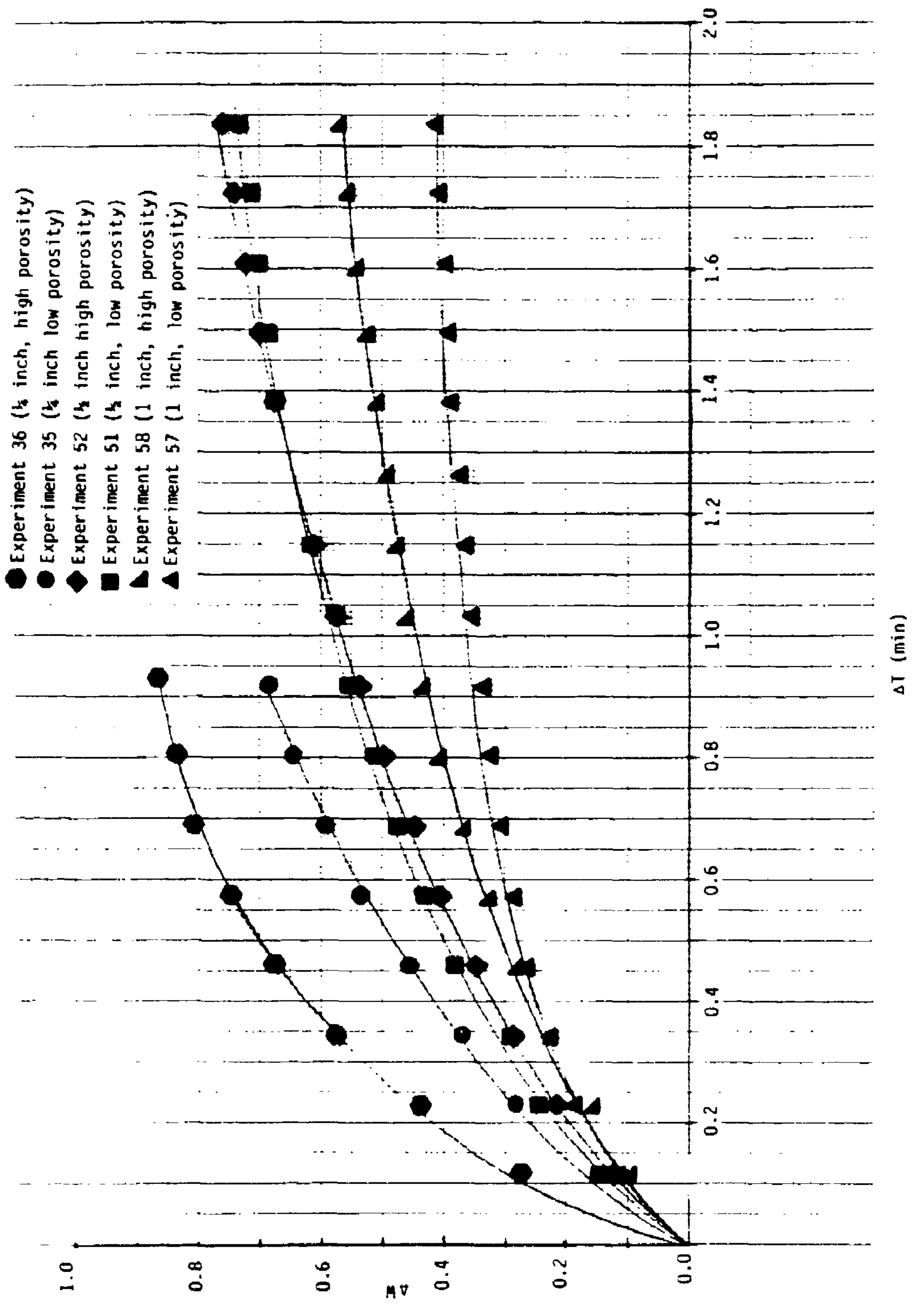

FIGURE 13. EFFECT OF COUPON THICKNESS ON PENETRATION OF WATER INTO MORTAR

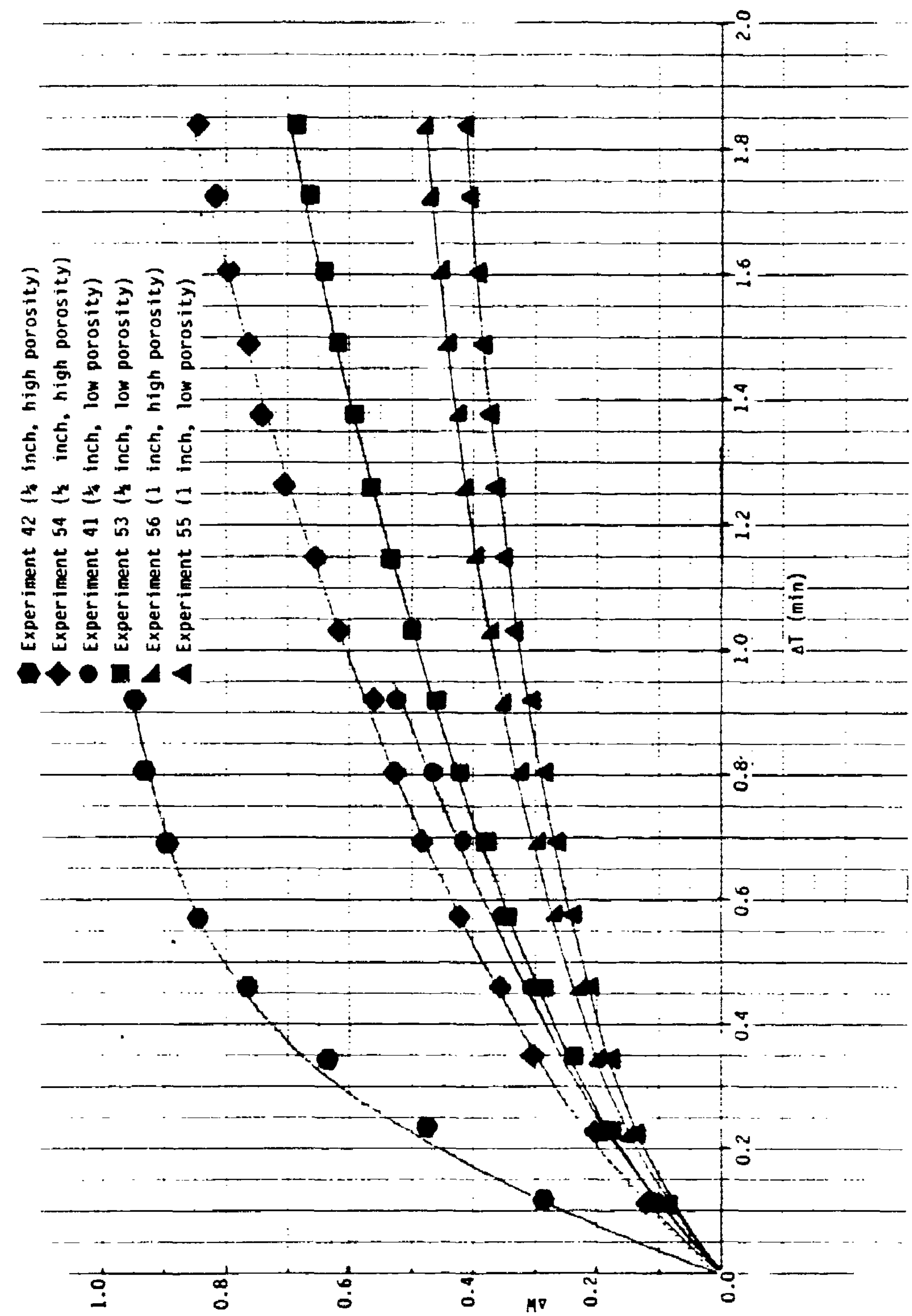

FIGURE 14. EFFECT OF COUPON THICKNESS ON PENETRATION OF 40 PERCENT DMSO/WATER INTO MORTAR

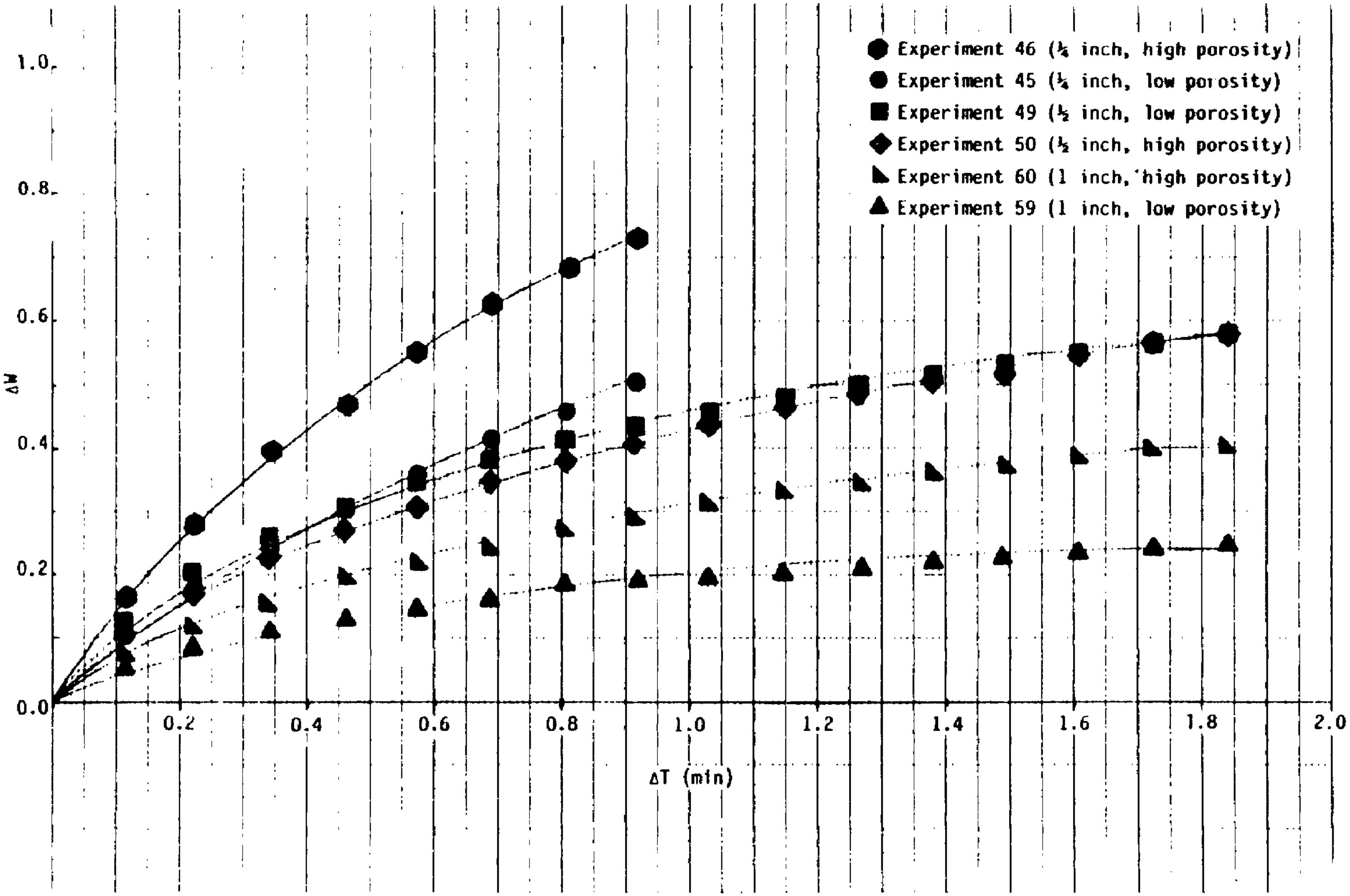

FIGURE 15. EFFECT OF COUPON THICKNESS ON PENETRATION OF 50 PERCENT ACETONE/WATER INTO MORTAR

material to the other becomes more tortuous due to an increased path length. In a heterogeneous material such as concrete, paths through the pore structure may also be blocked such that the number of paths which allow travel completely through the material are reduced. An increased path length which is more tortuous and contains blocked pores would tend to decrease the penetration rate as was shown experimentally. It is important to note that pores inaccessible to the decontaminating solution as a result of blockage would also be inaccessible to the agent or explosive containment.

4.2.4.2 FREON 113. Attempts made to spray FREON 113 on 1/4-inch high and low porosity mortar coupons failed. The weight gain from FREON adsorption was impossible to measure because the FREON 113 would evaporate from the coupon before the coupon could be weighed. The application of FREON 113 by the spraying method does not appear feasible and, as such, further experiments involving spraying FREON 113 were not performed.

4.2.4.3 MEA Solution. Spraying tests were conducted using a 50 percent aqueous solution of MEA, a candidate CW agent decontaminant. The results of the Experiments 64 through 69 using high and low porosity coupons of 1/4-inch, 1/2-inch, and 1-inch thickness are shown in Figure 16. Comparison of Figure 16 with Figures 13, 14 and 15 indicates the same general trends prevail for the aqueous MEA solution as for the other water-organic solutions.

4.2.5 Comparison of Experimental Data with Capillary Flow Theories

The experimental data was compared with theoretical equations which predict the rate of movement of fluids through porous media to determine if a correlation exists. One such equation is the Washburn equation(1). This equation considers capillary action as the driving force in penetrating a horizontal, cylindrical capillary (simulating the pores within mortar). The depth of penetration is given as:

$$L^2 = \frac{r\,t\,\gamma\,\cos\theta\;g_c}{\eta}$$

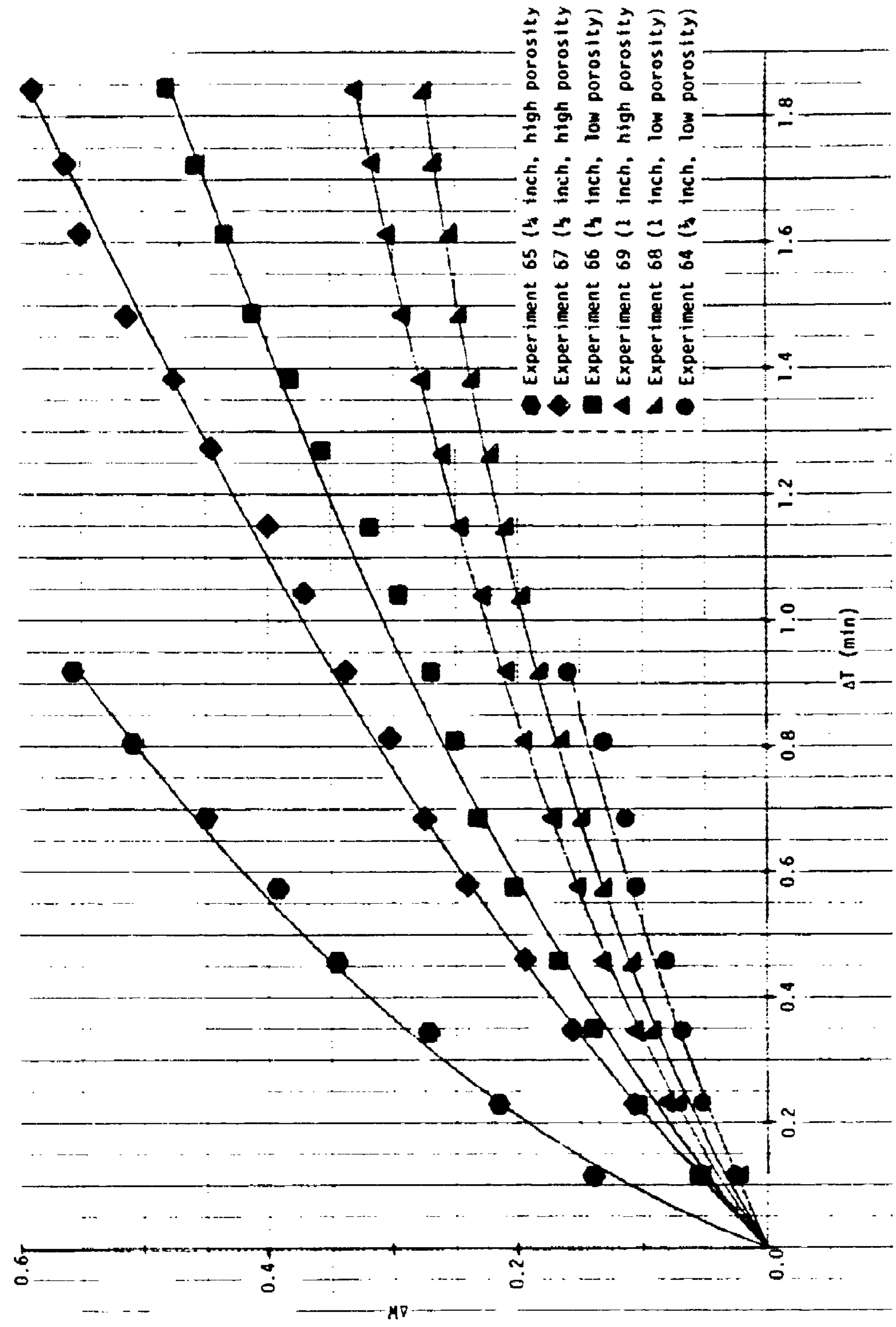

FIGURE 16. EFFECT OF COUPON THICKNESS ON PENETRATION OF 50 PERCENT MEA/WATER INTO MORTAR

where

L = depth of penetration (cm)

τ = tortuosity of the porous material = $1/\epsilon$ for many porous materials (ϵ = porosity) (Reference 2)

t = time (sec)

γ = surface tension of liquid decontaminant (dyne/cm)

θ = contact angle (the angle of contact is small for most liquids. Therefore, it is assumed that $\cos\theta = 1$.)

η = viscosity of the liquid (cp)

g_c = 1 gm cm/dyne sec^2

The above equation can be used to calculate a theoretical time of penetration of a 1/4 inch (0.635 cm) mortar coupon by water as follows:

$$(0.635)^2 = \frac{5.4^* \times t \times 72 \times 1 \times 1}{1.0}$$

$$t = 0.001 \text{ seconds}$$

Because this calculated time is much less than the experimental time (about 15 minutes for penetration in Experiment 18), the Washburn equation is not applicable to such a complex material such as mortar.

Another theory which reportedly predicts the rate of moisture movement in a porous medium is the water absorption law[3]:

$$\Delta W = A \Delta T^{\frac{1}{2}}$$

where ΔW = mass of water absorbed

A = constant

ΔT = time

Because this equation is used to predict unsaturated flow, only the experimental absorption rates of the 1-inch coupons and the first few sprayings of the 1/2-inch and 1/4-inch tests can be compared. A plot of ΔW versus $\Delta T^{\frac{1}{2}}$ using experimental data obtained in spraying of 1 inch mortar coupons with

* Porosity of coupon used in experiment 18 is 18.6 percent. Thus, ϵ = 1/0.186 = 5.4.

water is presented in Figure 17. As shown, the relationships are initially linear but diverge from linearily as the mortar becomes more saturated. Figure 17 also shows a dependence of the penetration rate on the coupon porosity since the data does not fall on a single curve. Porosity is not taken into account in the water absorption law.

Anotner variable which affects the penetration rate but is also not included in the water absorption law is the surface tension. Thus a correlation representing the rate of penetration of a liquid into mortar should include terms for $\Delta T^{1/2}$, the surface tension (τ) and the coupon porosity (ϵ) as follows:

$$\Delta W = A\Delta T^{1/2} + B\tau + C\epsilon$$

where A, B and C are constants.

Further efforts are required to determine the constants A, B and C such that the experimental dat. obtained from spraying various liquids on mortar can be integrated into one correlation.

4.3 Spraying Application Conclusions

Results from the spraying experiments indicate that:

- the penetration rate of liquid into mortar increases with an increase in porosity;
- the penetration rate of liquid into mortar increases with an increase in the surface tension of the liquid. As such, surfactants which lower the surface tension (e.g., Triton X-100) should not be used when decontaminating concrete;
- trends are independent of the porosity of the coupon;
- an increase in the coupon thickness caused a decrease in the penetration rate, presumably because of an increase in path length through the coupon and an increase in blocked pores inaccessible to the solution;

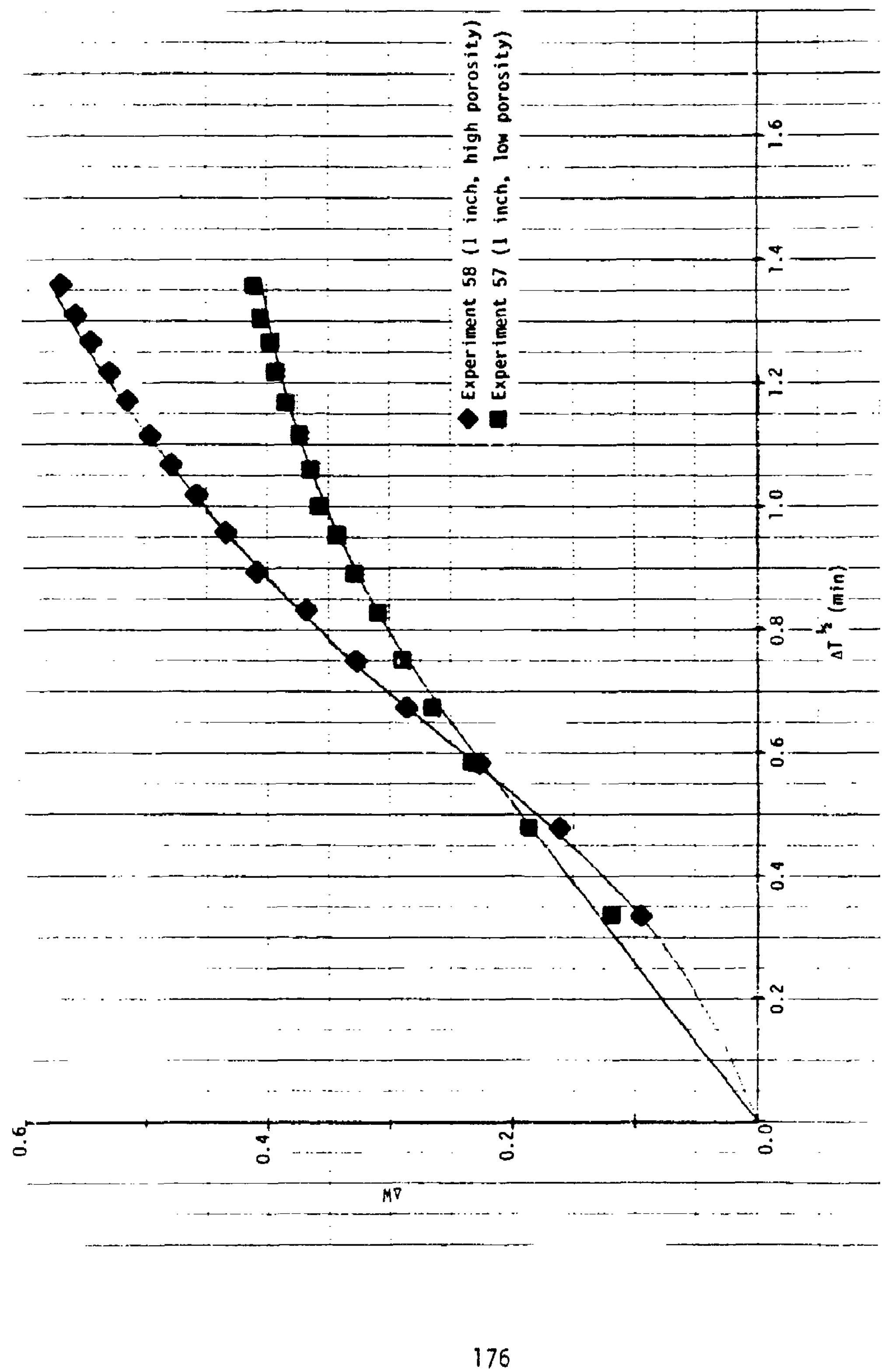

FIGURE 17. CORRELATION OF EXPERIMENTAL DATA (WATER/1-INCH COUPON) WITH THE WATER ABSORPTION LAW

- application of aqueous solutions (e.g., water, water/co-solvents (e.g., DMSO, acetone) and water/MEA) by spraying is feasible if the depth of contamination is less than 1/2 to 1 inch;
- application of liquid FREON 113 by spraying does not appear feasible.

The following parameters are preferred for application of a liquid to concrete.

- Spray nozzle type - coarse sized water particles
- Supply pressure - 100 psig (6.8 atm)
- Coverage - 0.05 gal/ft^2/spray (2.0 liter/m^2/spray)
- Spray cycle interval - about 5 minutes (lower times may be required for solutions of volatile solvents).

The above parameters will be used for subsequent decontamination experiments involving liquid decontaminants in both Tasks 3 and 4. The parameters will also be used as the basis for engineering/economic analyses if a liquid decontaminant concept survives the experimental screening procedures.

5.0 NH_3 DIFFUSION EXPERIMENTS

The NH_3 gaseous diffusion experiments were undertaken to determine the rate of diffusion of NH_3 gas (candidate decontaminant for GB, VX and HD) through mortar coupons.

5.1 Description of Diffusion Experiments

5.1.1 Diffusion Apparatus

The NH_3 diffusion apparatus is illustrated in Figure 18. The apparatus consisted of two chamber halves, between which a mortar coupon was placed. O-rings and bolts between the chamber halves served to seat the coupon firmly in place. The NH_3 side of the chamber, through which a flow of NH_3 gas was maintained, included a propeller which enhanced mass transfer of NH_3 from the bulk gas phase to the coupon surface. A nitrogen flow was

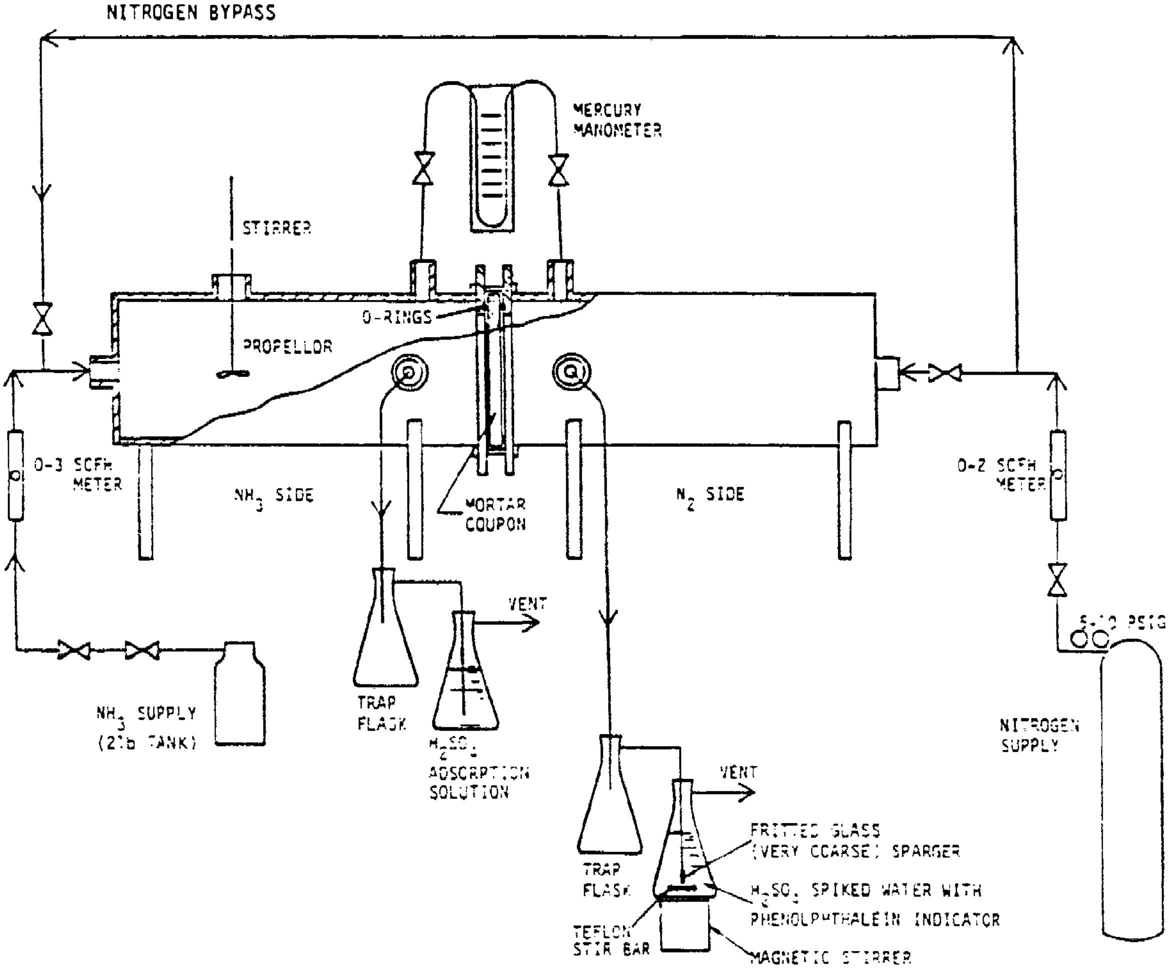

FIGURE 18. NH_3 DIFFUSION APPARATUS

maintained through the N_2 side of the chamber. The nitrogen flow from the chamber was passed through an acidic solution containing phenolphthalein indicator. The acid solution served to absorb any NH_3 that had diffused through the coupon. A fritted glass sparger and magnetic stirrer were used to disperse the nitrogen stream into small bubbles to aid absorption of the NH_3 into the solution. On the NH_3 side, a H_2SO_4 solution absorbed any excess NH_3 flow to prevent venting of NH_3 up the hood.

A mercury manometer was used to measure the pressure differential across the coupon. Rotameters were used to measure the NH_3 and N_2 flow rates.

5.1.2 Test Variables/Data

In the gaseous diffusion tests, only the coupon thickness (1/4, 1/2 or 1 inch) and mortar type (high or low porosity) were varied. All other parameters such as the N_2 flow rate and supply pressure, the NH_3 flow rate and supply pressure; and the propeller speed were maintained relatively constant throughout the experiments.

5.1.3 Test Procedure

In the gaseous diffusion experiments, a concentration of NH_3 near 100 percent was maintained on the NH_3 side of a mortar coupon by continuously flowing NH_3 through one side of the chamber. NH_3 which had diffused through the coupon was continuously removed by a nitrogen purge stream thereby maintaining the NH_3 concentration on the N_2 side of the mortar coupon near zero percent. The nitrogen purge was passed through water containing phenolphthalein. The water was acidified with a known amount of H_2SO_4. The rate and total amount of NH_3 diffusing through the coupon were determined by noting the time required to neutralize the acid solution containing the known amount of acid. Thus, the NH_3 which had diffused through the coupon was used to directly titrate the acid solution.

The following procedure was used in conducting the NH_3 diffusion experiments:

1. Select and record coupon number, thickness (¼, ½ or 1 inch) and porosity (high or low)

2. Place coupon between chamber halves and bolt chamber halves together
3. Prepare absorber solutions as follows:
   - NH_3 side: add about 100 to 150 ml of concentrated H_2SO_4 to about 900 ml of tap water
   - N_2 side: add several drops of phenolphthalein solution to 400 ml of de-ionized water
4. Start N_2 flow at about 2 scfh at a supply pressure of about 5 to 10 psig
5. Start propeller
6. Start NH_3 flow at a flow of about 1.3 scfh.
7. Note time when N_2 side absorption solution turns a faint pink in color (initial breakthrough of NH_3)
8. Replace N_2 side absorption solution with fresh solution containing about 400 ml of de-ionized water, several drops of phenolphthalein solution and 1.000 ml of 0.100 $\underline{N}$ H_2SO_4 solution (H_2SO_4 solution measured by pipet)
9. Repeat steps 7 and 8 increasing the amount of spiked H_2SO_4 as required
10. Terminate experiment when two to three consecutive solutions containing the same quantity of 0.1 $\underline{N}$ H_2SO_4 require the same time period to turn a faint pink in color
11. Monitor pressure differential across chamber halves, NH_3 flow rate, N_2 flow rate and time throughout the experiment
12. At completion of experiment turn off NH_3 flow and purge NH_3 side of chamber with dry nitrogen.

A variation in the above procedure was required in Experiment 9 involving the one inch thick, low porosity coupon. It was necessary to stop the ammonia and nitrogen flows several times during the experiment because of the duration of the experiment (i.e., Experiment 9 required about 75 hours to reach approximate steady-state conditions). When the experiment was stopped

and the system allowed to stand over-night, the gas flows were stopped, inlet and outlet valves on both the ammonia side and the nitrogen side were closed. On the following morning, the flows were re-started and sampling was initiated after the nitrogen side was purged (about 15 minutes).

5.2 Discussion of NH_3 Diffusion Results

The results of the NH_3 diffusion experiments are discussed in the following sections. Actual data obtained from the experiments are given in Battelle Laboratory Recordbooks Nos. 39109 and 39265.

Eleven ammonia diffusion experiments were conducted in the test apparatus shown in Figure 18. Penetration of the coupons by ammonia was achieved in all of the experiments. Times for the ammonia gas to penetrate mortar coupons (1/4, 1/2 and 1 inch thick of low and high porosity), times to reach approximate steady-state conditions and effusion rates* were obtained.

5.2.1 Data Analysis Method

During the diffusion experiments, the rate of which ammonia gas effused from one side of a mortar coupon was determined. The effusion rate was calculated from the time required for a known amount of acid to be neutralized by the effused ammonia. For example, in Experiment 4 , eight minutes were required for a solution containing one mL of 0.1 N sulfuric acid to be neutralized (solution turned a faint pink in the presence of phenolphthalein indicator). The effusion rate was then calculated as follows.

* The effusion rate is the rate by which the ammonia gas was emitted from the coupon on the side opposite to that subjected to 100 percent ammonia gas. At steady-state conditions, the effusion rate of NH_3 from the coupon equals the rate of diffusion of NH_3 through the coupon.

NH_3 in sample (millimoles)	=	Normality of sulfuric acid x mL spiked
	=	0.1 x 1 = 0.1 millimoles
Effusion rate (millimoles/min)	=	millimoles NH_3/sample time
	=	0.1/8 = 0.0013

The time required to reach approximate steady-state conditions was determined by comparison of the effusion rates from two to three consecutive samples. Steady state was assumed when the effusion rates for the two consecutive samples were essentially the same.

The effusion rate was determined over a particular sampling period during an experiment. Hence, a knowledge of the total amount of ammonia which had effused from the coupon up to the start of the particular sampling period is not required. As such, incomplete data obtained from experiments which ran overnight were still applicable.

5.2.2 Diffusion Results

Results of the diffusion experiments are illustrated in Figure 19 (1/4 inch coupons), Figure 20 (1/2 inch coupons) and Figure 21 (1 inch coupons). Analysis of the plots indicate that the time to penetration, the effusion rate, and the time to reach steady-state increased with either an increase in coupon thickness and/or a decrease in coupon porosity. This trend is further illustrated by ranking of the various coupons in relation to the steady-state effusion rate. The ranking, in order of highest to lowest effusion rate, is as follows.

1/4" - high* >1/2" - high >1/4" -low >1" -high >1/2" - low> 1" - low

* Denotes porosity as determined by the water/cement ratio used to prepare the coupons (see Section 3.2).

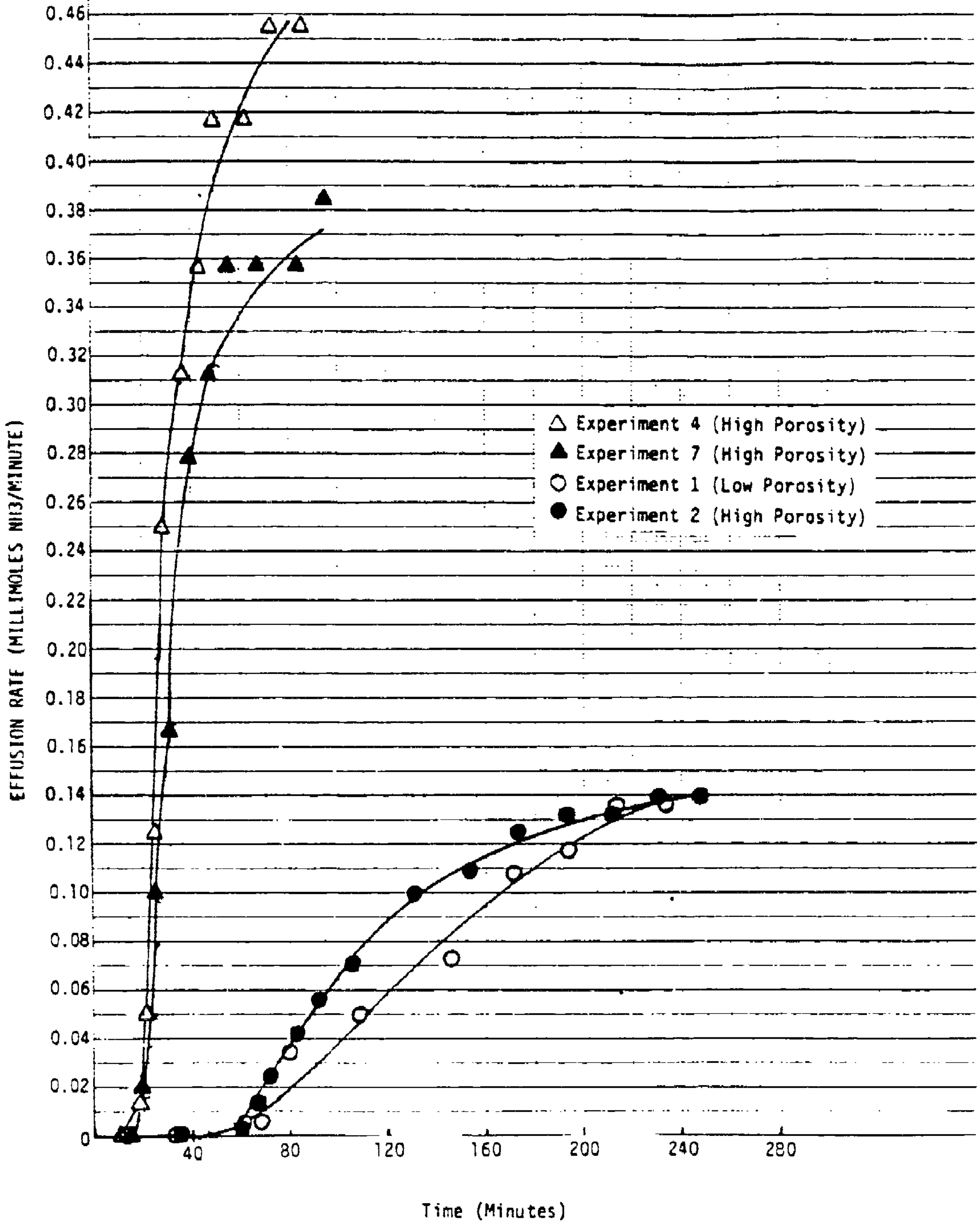

FIGURE 19. NH_3 DIFFUSION RESULTS - 1/4-INCH COUPONS

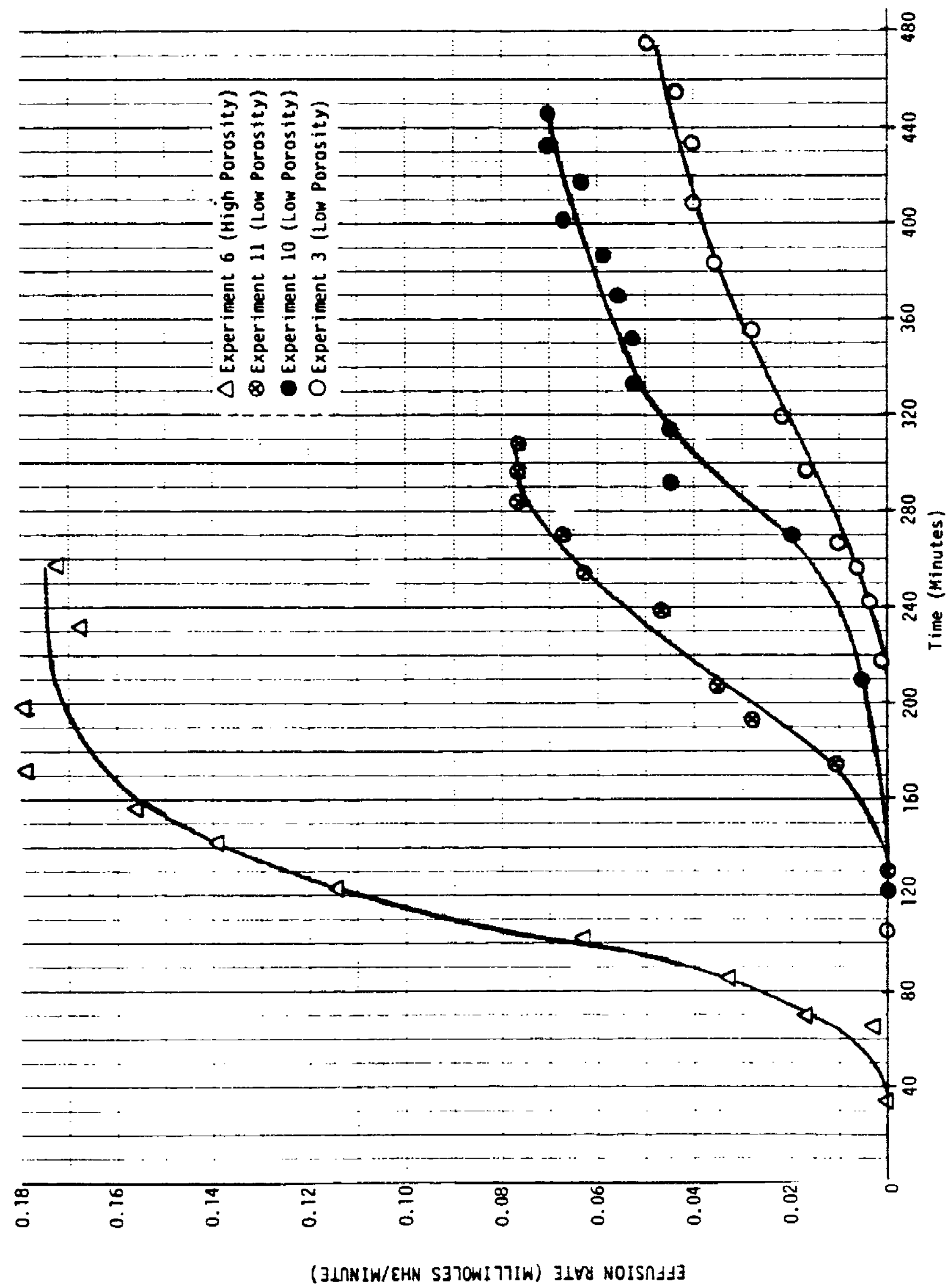

FIGURE 20. NH_3 DIFFUSION RESULTS - 1/2-INCH COUPONS

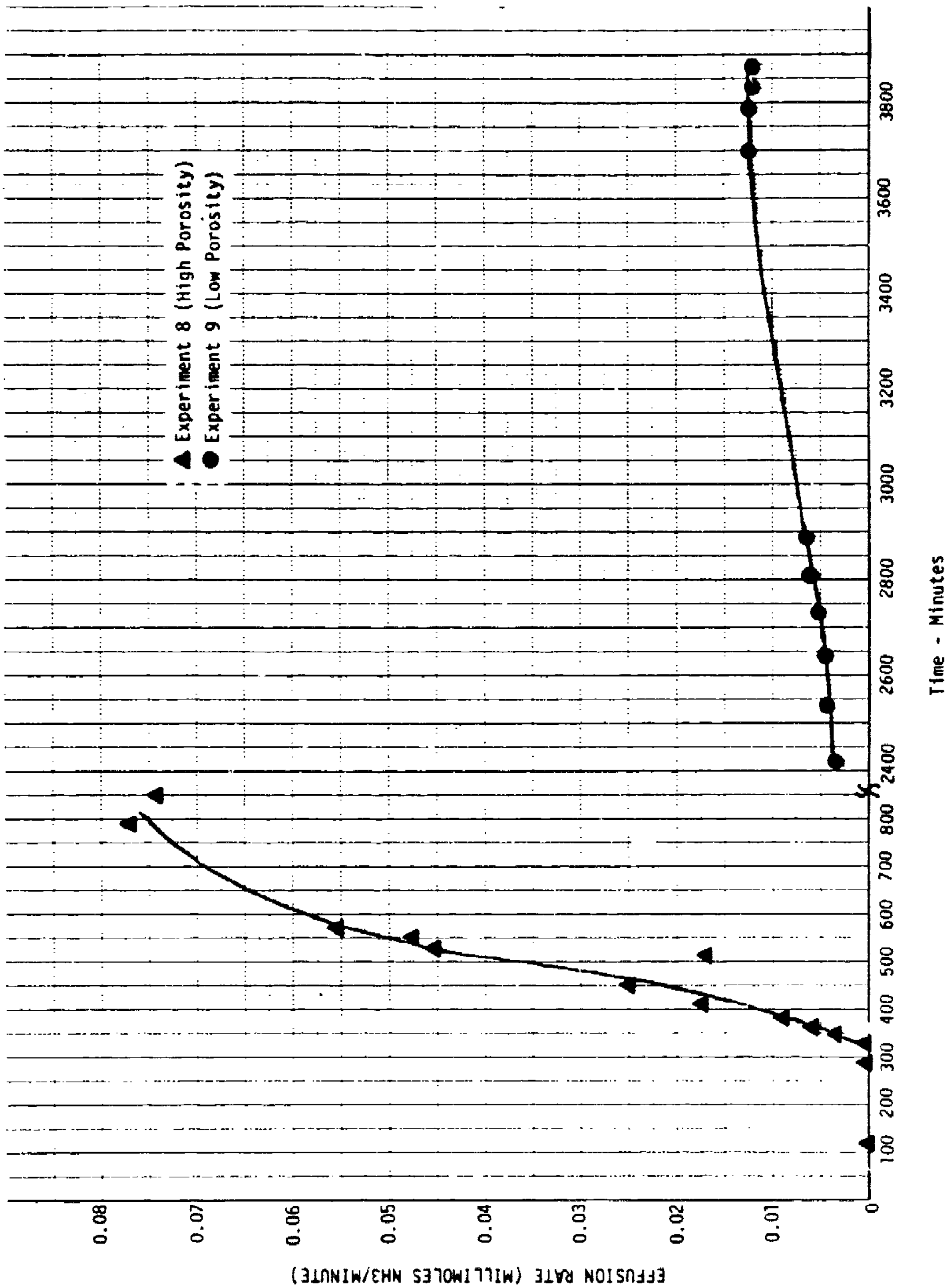

FIGURE 21. NH_3 DIFFUSION RESULTS - 1-INCH COUPONS

A summary of the results abstracted from Figures 19 through 21 is given in Table 5. Also shown in Table 5 are experimentally determined porosities of the coupons used in each test and the average pressure differential between the ammonia and nitrogen sides of the chamber recorded during each test. The pressure differential values indicate that the ammonia gas was diffusing against a pressure gradient in most of the experiments.* As such, the results obtained in these experiments may have yielded slightly conservative effusion rates and penetration times.

Experimental results from the spraying experiments indicate that the complexity of the pore structure in mortar appears to be dependent on the thickness of the coupon tested (see Section 4.2.4.1). The pore matrix appears to become more complex as the thickness of the coupon is increased. This trend is also apparent on analysis of the data obtained from the ammonia diffusion tests. Figure 22, a plot of the steady-state effusion rate versus coupon thickness, indicates that the steady-state effusion decreases in proportion to coupon thickness. If complexity of the pore matrix is not a factor, then similar steady-state effusion rates should be observed for coupons of similar porosity and plots of the effusion rate versus coupon thickness should yield nearly horizontal curves. This is in contrast to the experimental curves shown in Figure 22.

Thus, when extrapolating the results obtained during these experiments to field concrete matrices, it is important to consider not only the porosity of the concrete but also the water/cement ratio used to prepare the concrete and the thickness of the concrete.

5.2.3 Comparison of Experimental Data with Diffusion Theories

Two approaches may be used to calculate the steady-state diffusion rate of ammonia through concrete. In the first method, the mean free path of

* A positive pressure gradient (i.e. pressure higher on the ammonia side than on the nitrogen side) was observed in the first half of Experiment 1 due to the back pressure caused by the sparger on the ammonia side NH_3 absorption flask. Removal of the sparger, which did not affect the results, allowed the use of a decreased NH_3 supply pressure. This in turn, reduced the pressure differential.

TABLE 5. SUMMARY OF EXPERIMENTS FOR THE MEASUREMENT OF THE DIFFUSION RATE OF NH_3 THROUGH MORTAR COUPONS

Expt No.	Mortar Coupon Thickness (in)	Porosity	Experimental Porosity (Vol %)	Penetration Time (min)	Time to Steady-State (min)	Steady-Sate Effusion Rate $\left(\frac{\text{Millimoles } NH_3}{\text{min}}\right)$	Average[a] ΔP (mmHg)
1	1/4	Low	11.6	14	214	0.136	Varied
2	1/4	Low	11.6	33	230	0.139	-3
3	1/2	Low	12.9	105	$>$ 475	$>$ 0.050	-4
4	1/4	High	17.4	11	73	0.455	-4
5[b]	1/4	High	-	-	-	-	-
6	1/2	High	15.9	35	171	0.179	-10
7	1/4	High	17.1	15	96	0.385	-10
8	1	High	14.1	123	786	0.077	-10
9	1	Low	10.1	1269-2178	~ 3700	0.013	negative
10	1/2	Low	15.2	122	432	0.071	-23
11	1/2	Low	15.7	130	283	0.077	-19

(a) A negative sign indicates the pressure on the nitrogen side of the chamber was higher than the pressure on the ammonia side of the chamer.

(b) Experiment 5 was unsuccessful because of a crack in the mortar coupon.

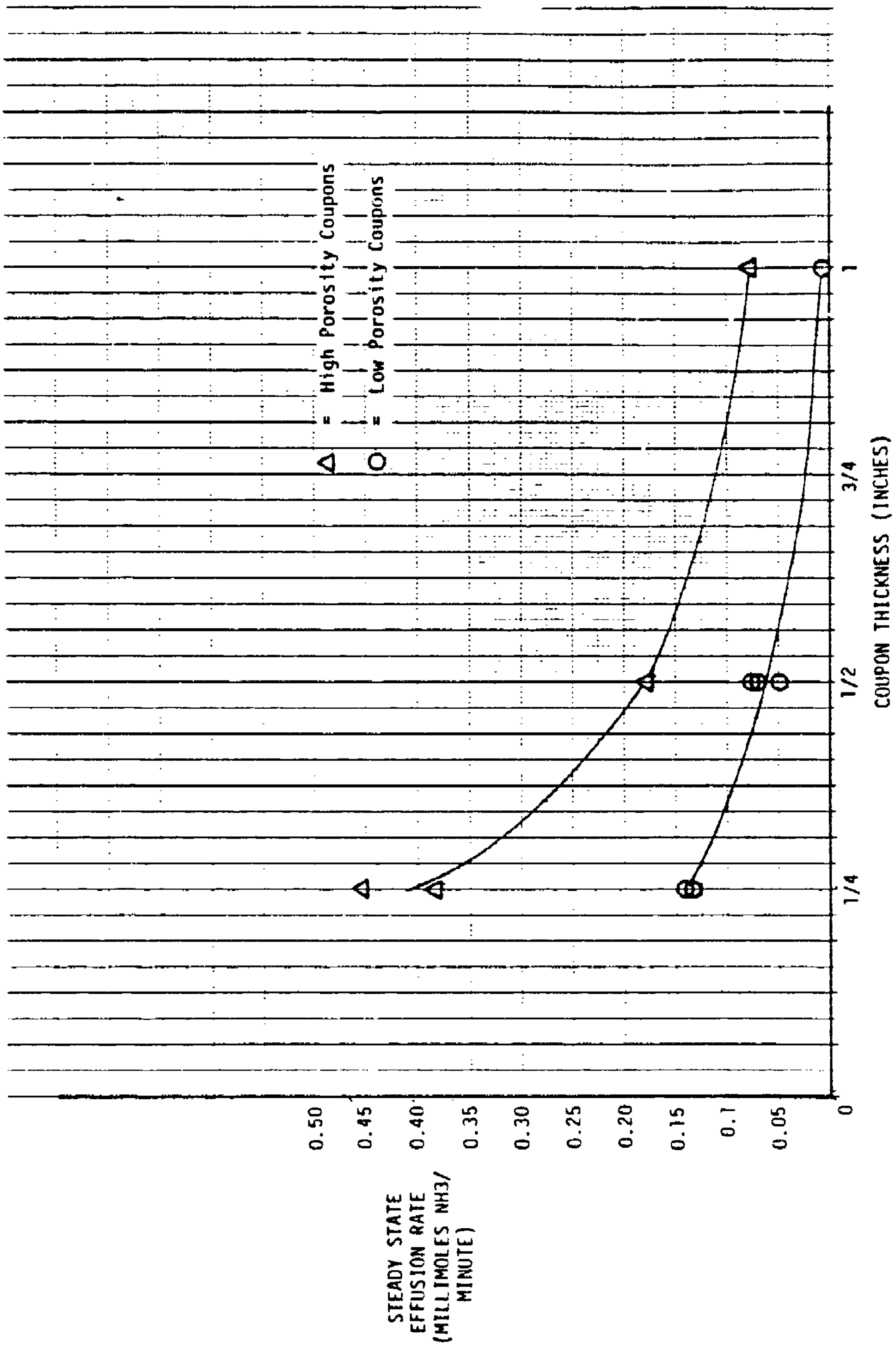

FIGURE 22. EFFECT OF COUPON THICKNESS ON THE EFFUSION RATE OF NH_3

the gaseous molecule and the average pore size of the solid are considered. In the second method an effective diffusivity is estimated using the porosity of the solid

5.2.3.1 Steady-State Diffusion-Method 1 The diffusion of gases through solids is dependent upon the diameter of pores or capillaries in the solid. The average pore diameter will determine the type of diffusion process occurring (i.e. Knudsen, molecular or transition Region diffusion) as follows.

The type of diffusion process can be determined by comparing the mean free path (λ) of the gas molecules with the average pore diameter (d) of the solid. If $\lambda/d > 10$, then the diffusion is in the Knudsen regime. If $\lambda/d < 0.01$, then the diffusion is in the molecular regime. Values of λ/d between 0.01 and 10 indicate the diffusion process is in the transition regions.

The mean free path, which is the average distance a molecule travels before it collides with another molecule, is given by:

$$\lambda = \frac{3.2\,\mu}{p}\sqrt{\frac{RT}{2\pi g_c M}}$$

Where, for NH_3,:

M = 17 gm/gm-mole

R = 84,780 gm-force cm/ gm-mole K

g_c = 980 gm cm/gm force sec^2

P = 1 atm = 1033.2 gm force/cm^2

T = 25c = 298 K

μ = 1,006 x 10^{-4} poise

Solving gives $\lambda = 4.84 \times 10^{-6}$ cm.

Well-cured concrete specimens have been reported to contain gel pores having a mean diameter about 0.4 x 10^{-6} inch connecting larger capillary

pores. It is assumed that the mortar specimen used in the diffusion tests have an average pore diameter of about 1×10^{-6} cm. Thus, $\lambda/d = 4.8$ indicating the diffusion process is in the transition regime. It can be shown that the following equation applies for transition regime equimolar counter diffusion:

$$N_a = \frac{PA(X_{A2} - X_{A1})}{RT\ (Z_2 - Z_1)} \times \frac{1}{(1/D_{AB} + 1/D_{KA})}$$

Where

N_a = diffusion rate of NH_3 (gm-mole/sec)
P = 1 atm
X_{A2} = 1 (100 percent NH_3 on ammonia side of the coupon)
X_{A1} = 0 (0 percent NH_3 on nitrogen side of the coupon)
A = Area of coupon exposed to ammonia
= 81.07 cm^2 (4 inch diameter circle)
R = 82.057 cm^3 atm/gm-mole K
T = 298 K
Z_2-Z_1 = 0.635 cm (1/4 inch)
D_{AB} = 0.230 cm^2/sec (Reference 4)
D_{KA} = $9.7 \times 10^3\ (d/2)\ \sqrt{T(K)/M}$

= 0.020 cm^2/sec

Solving gives $N_a = 9.6 \times 10^{-5}$ gm-mole/sec. Experimental steady-state diffusion rates ranged from 7.6×10^{-6} gm-moles/sec (Experiment 4) to 2.2×10^{-7} gm-moles/sec (Experiment 9). Thus, the theoretical diffusion rate is one to two orders of magnitude larger than the experimentally determined diffusion rate.

5.2.3.2 Steady-State Diffusion - Method 2. A second approach which can be used to calculate a diffusion rate for ammonia through concrete molcules is the use of Ficks law and an effective diffusivity as follows.

Ficks Law $N_a = AD_{eff} \cdot \frac{dC_A}{dZ} = \frac{A\ D_{eff}}{RT} \cdot \frac{dP_A}{dZ}$

Where

P_A = partial pressure of ammonia (atm)
D_{eff} = effective diffusivity

Ficks law can be integrated to give

$$Na = \frac{A \Delta P_A\ D_{eff}}{RT\ (Z_2 - Z_1)}$$

Where P_A = difference in partial pressure of ammonia across the coupon = (1 atm-0) = 1 atm

D_{eff} can be expressed as follows:

$$D_{eff} = \frac{D_{AB}\ \varepsilon}{\tau}$$

Where ε = Porosity
τ = Tortuosity $\approx 1/\varepsilon$ (Reference 2)

The data from Experiment 1 inserted into the above equations yields:

$$N_a = \frac{81.07\ cm^2 \times 1\ atm \times 3.1 \times 10^{-3}\ cm^2/sec}{82.057\ cm^3\ atm/gm\text{-}mole\ K \times 298\ K \times 0.635\ cm}$$

$N_a = 1.6 \times 10^{-5}$ gm-mole/sec

This compares with an experimental value of 0.136 milligram moles/min = 2.3 x 10^{-6} gm mole/sec. Thus, the theoretical equation yields diffusion rates one order of magnitude higher than experimentally determined. Ficks law may be modified to represent experimental data if a factor of 0.1 is applied. The resulting equation, assuming $P_A = 1$ and T = 298K, is as follows:

$$\text{Na (gmmoles } NH_3/cm^2 \text{ sec)} \simeq \frac{\varepsilon^2 \times 10^{-6}}{\text{Sample thickness (cm)}}$$

If the use of ammonia gas is selected as a candidate method for CW decontamination field testing, then this equation may be used as a first approximation of the steady-state diffusion rate of ammonia into concrete.

5.3 NH_3 Application Conclusions

Results from the ammonia diffusion experiments indicate that:

- application of ammonia gas, a candidate CW agent decontaminant,to concrete matrices greater than one inch deep appears feasible;
- the magnitude of the diffusion rate is dependent upon the porosity and thickness of the sample (i.e., the diffusion rate increases with an increase in the porosity but decreases with depth;
- the steady-state diffusion rate of ammonia through mortar can be approximated with a correlation containing factors for porosity and thickness of the sample.

Data obtained from the ammonia diffusion experiments will be used in subsequent subtasks in Task 3 if further testing (beyond the prescreening performed in Subtask 3) of the decontamination effectiveness of ammonia gas is required.

6.0 CONSTANT CONTACT EXPERIMENTS

The constant contact experiments investigated the rate of penetration of a liquid into mortar under conditions of method of fluid application different from the spraying method. The constant contact method continuously subjected the surface of the mortar coupon to the decontaminating solution. As such, the application of a decontaminant in the form of a foam or gel can be simulated by the constant contact method. The knowledge gained from the constant contact experiments will help to determine the conditions needed to decontaminate concrete sumps using liquid decontaminants.

6.1 Description of Constant Contact Experiments

6.1.1 Constant Contact Apparatus

The constant contact apparatus, shown in Figure 23, was designed to maintain a constant liquid - solid interface on one side of the test coupon while leaving the other side open for monitoring the appearance of moisture. Other design considerations were

- keeping the hydrostatic head as small as possible,
- closely monitoring the level of liquid with the level indicator,
- accurately measuring the amount of liquid added by using a buret to add liquid,
- keeping losses due to evaporation from the chamber to a minimum by making all openings in the chamber as small as possible
- utilizing a coupon holder configuration similar to the one used for the gaseous diffusion experiments.

6.1.2 Test Variables/Data

In the constant contact experiments, only the coupon thickness (1/4, 1/2 or 1 inch), mortar type (high or low porosity) and test solutions/

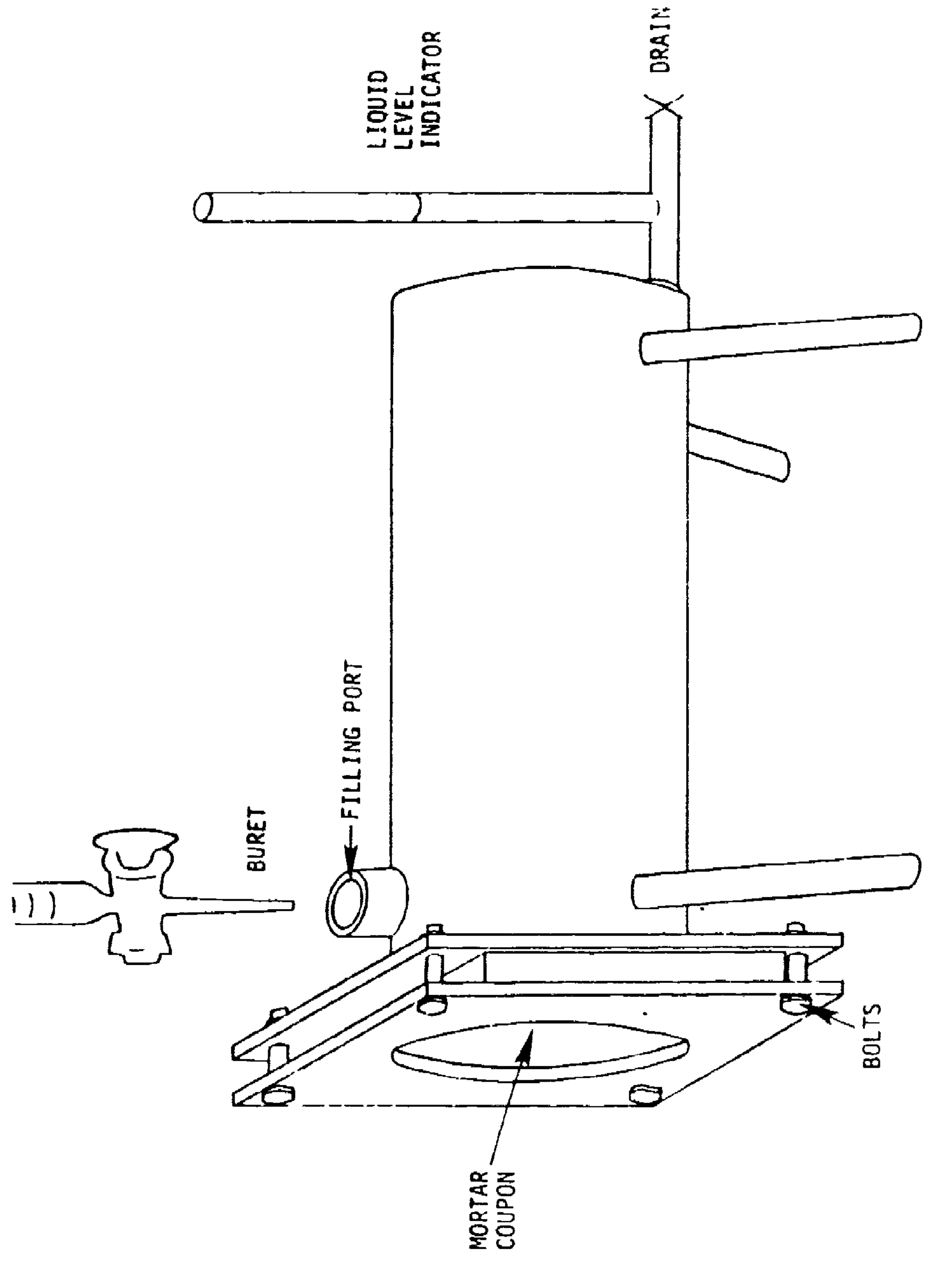

FIGURE 23. CONSTANT CONTACT APPARATUS

solvents were varied. All other parameters conditions such as level of liquid in the chamber were maintained relatively constant for all experiments (e.g. ambient room temperature and humidity).

6.1.3 Test Procedure

A mortar coupon, fully cured and equilibrated to ambient room conditions, was placed in the experimental apparatus. The chamber was then filled with solution or solvent and the time recorded. As liquid from the housing was absorbed into the mortar, make-up liquid was added to the housing through a buret to maintain a constant liquid level in the housing. The time when solution or solvent was first detected on the dry side of the test coupon was recorded. The experiment was continued until approximatly by a steady-state flow through the mortar coupon was achieved.

The following are more detailed steps in the procedure used when conducting the constant contact experiments:

1. Select and record solution, coupon thickness (¼, ½ or 1") and coupon porosity (high or low)
2. Record initial coupon weight
3. Install coupon in apparatus
4. Fill apparatus and buret with selected solution
5. Record starting time and buret reading
6. When liquid level falls below the mark on the liquid level indicator attached on the side of the chamber, refill to the mark and record the time and the buret reading
7. Record time from start of the experiment to the time of the latest addition of solution and amount of solution added
8. Repeat the steps 6 and 7 until the rate of liquid added is constant
9. Note when breakthrough occurs and the approximate percent coverage of wet surface.

6.2 Discussion of Constant Contact Results

The results of the constant contact experiments are discussed in the following sections. Actual data obtained from the experiments are given in Appendix D and Battelle Laboratory Recordbooks Nos. 39109 and 39265.

The constant contact experiments involved continuous exposure of one surface of mortar coupons to a decontaminating solution. There is a significance difference between the spraying and constant contact methods. In spraying, a film of liquid is formed on the surface from which liquid is drawn into the pores of concrete through, primarily, capillary action. In contrast, liquid in the constant contact method is also forced into the pores by a hydrostatic pressure gradient and Darcy's Law becomes the primary mechanism by which liquid enters the pores.

6.2.1 Data Analysis Method

The primary data recorded during the constant contact experiments was the volume of solution added to the apparatus (ΔV) over a period of time (ΔT). ΔV represents the quantity of solution that penetrated into the coupon, evaporated from the filling port of the test apparatus (minor amount) and/or evaporated from the coupon after complete penetration was achieved. A direct measurement of the coupon weight change versus time as was done in the spraying tests was not possible because of the configuration of the constant contact apparatus. When the data was analyzed to determine penetration rates, evaporation was neglected when the rate data (ΔV versus ΔT) limited to the initial stages of the experiment (i.e., prior to complete penetration of the coupon). After complete penetration was achieved, analysis of the data to determine a steady-state rate becomes difficult because evaporation was assumed to affect the penetration rate.

6.2.2 Constant Contact Results

Sample curves of ΔV versus ΔT for the experiments involving 1/4 inch low and high porosity coupons are shown in Figure 24 and 25,

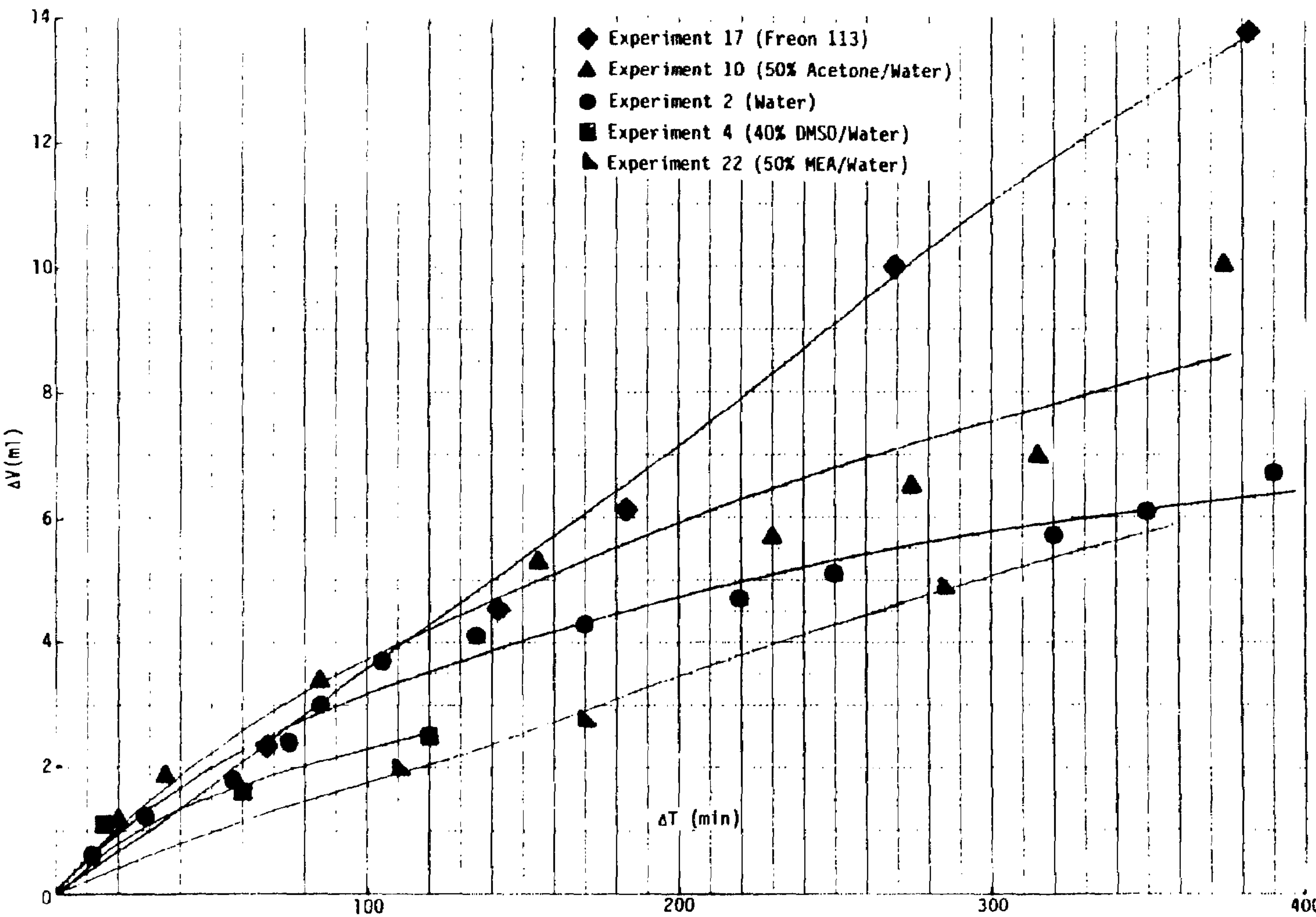

FIGURE 24. CONSTANT CONTACT TEST RESULTS (1/4-INCH LOW POROSITY COUPONS)

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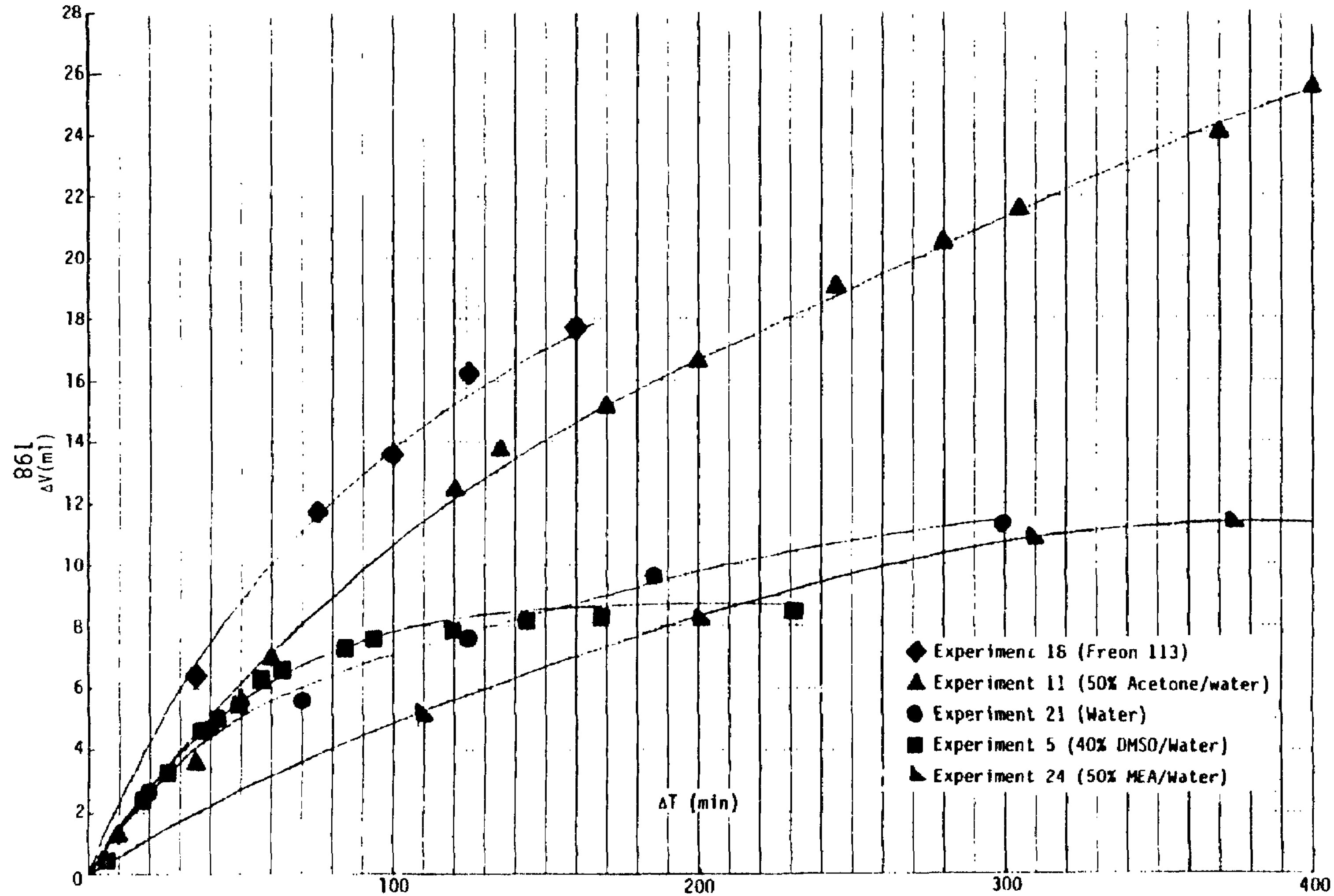

FIGURE 25. CONSTANT CONTACT TEST RESULTS (1/4-INCH HIGH POROSITY COUPONS)

respectively. Similar curves (see Appendix D) were obtained for the other types of coupons (1/2 and 1 inch low and high porosity). Figures 24 and 25 indicate that the initial rate of penetration is approximately the same for all solutions after which time the rates tend to diverge. It appears that the divergence of the rates may be caused by evaporation effects. For example, the divergence of the FREON and 50 percent acetone rates from the water, 40 percent DMSO and 50 percent MEA curves may be due to the high evaporation rates of FREON and acetone from the coupons. Evaporation test results (see Section 7.2) indicate that for high porosity coupons, FREON and 50 percent acetone have the highest evaporation rates of the solutions tested.

A summary of the penetration rates during the initial stages of each experiment and the time required for the liquid to completely penetrate the coupon are shown in Table 6. It was initially anticipated that more rapid penetration times and higher rates would be observed for the constant contact experiments than for the spraying experiments. However, an analysis of the data indicates that similar results were obtained. A comparison of the data from the spraying and constant contact experiments involving water 40 percent DMSO, and 50 percent acetone solutions using 1/4 inch coupons is given in Table 7. The data indicates that the time required for the liquid to penetrate mortar coupons was less in the constant contact experiments than in the spraying experiments. However, the weight gained by the coupons was nearly identical over the same time period for the two application methods. As such, the constant contact method offers no distinct advantages over the spraying method. Moreover, the use of a gel or foam to hold the liquid in place may reduce the penetration rate below that observed in the constant contact experiments because of additional diffusional limitations imposed on the liquid by the gel or foam matrix.

A possible reason for the unexpectedly low effectiveness of the constant contact experiments is as follows. Several tests were performed in which coupons were totally immersed in water. Upon immersion, bubbles began forming at the pore openings at the surface of the coupon. The bubbles may have created an air interface at the pore openings which prevented and/or limited the penetration of liquid. Although bubble formation during the

TABLE 6. SUMMARY OF RESULTS FROM CONSTANT CONTACT EXPERIMENTS

Experiment Number	Solution	Coupon[a] Porosity	Coupon Thickness (Inches)	Penetration Rate (cc/min)	Time to Penetration (min)
2	Water	L	1/4	0.03	57
21		H	1/4	0.09	45
30		L	1/2	0.04	95 to 1075[b]
25		H	1/2	0.16	90
29		L	1	0.02	-
27		H	1	0.33	215 to 1123[b]
4	40% DMSO/Water	L	1/4	0.07	15
5		H	1/4	0.05	6
6		L	1/2	0.01	500 to 2103[b]
7		H	1/2	0.04	285
8		L	1	0.02	-
9		H	1	0.03	1245
10	50% Acetone/Water	L	1/4	0.03	155
11		H	1/4	0.11	60
13		L	1/2	0.03	285 to 940[b]
14		H	1/2	0.07	170 to 230[b]
15		L	1	0.02	-
16		H	1	0.06	-
17	FREON	L	1/4	0.03	142
18		H	1/4	0.15	75
19		L	1/2	0.09	75 to 1010[b]
28		H	1/2	0.15	125
20		L	1	0.05	-
23		H	1	0.09	2465?
22	50% MEA/Water	L	1/4	0.02	285
24	"	H	1/4	0.04	200

(a) L = Low porosity, H = High porosity

(b) The exact penetration time was not determined.

TABLE 7. COMPARISON OF RESULTS FROM SPRAYING AND CONSTANT CONTACT EXPERIMENTS

		Penetration Time(min)		ΔW[a]	
Solution	Coupon Porosity	Spraying	Constant Contact	Spraying[b]	Constant Contact[c]
Water	Low	86	57	0.28	0.15
Water	High	65	45	0.28	0.24
40% DMSO	Low	104	15	0.06	0.09
40% DMSO	High	83	6	0.05	0.04
50% Acetone	Low	156	155	0.40	0.46
50% Acetone	High	158	60	0.30	0.40

(a) $\Delta W = \dfrac{\text{Coupon weight at constant contact time of penetration- Initial Coupon Weight}}{\text{Saturated Coupon weight (from porosity tests) - Initial Coupon weight}}$

(b) The spraying experiments ΔW was abstracted from the data using the constant contact penetration time as the basis for comparison.

(c) ΔW for the constant contact experiments was calculated assuming the total amount of liquid added to the test appartus up to the time of penetration was absorbed by the coupon (i.e., no evaporation occurred).

spraying experiments may also occur, any bubbles which may have formed would have been displaced from the surface by the force of the spray.

In gel or foam applications, such bubble formation would reduce the effectiveness below that observed for the constant contact method due to the need for displacement of the bubbles not only from the concrete pores but also from the gel or foam. Because the constant contact method offers no distinct advantages over the spraying method, gel or foam application of liquid decontaminants to concrete materials is not recommended for further evaluation. However, decontamination of concrete sumps or pipes may be accomplished by the constant contact method. In this case, agitation would be beneficial, since it would cause displacement of the bubbles which impede the penetration of liquid into the pores.

6.2.3 Comparison of Experimental Data with Pressure Gradient Theory

The results from the constant contact experiments may be correlated with Darcy's law given as:

$$Q = KA\,(H/L)$$

where
- Q = flow rate of liquid through porous media
- K = coefficient of permeability for each media
- A = cross-sectional area
- L = length of diffusion
- H = head of the liquid

From the recorded data, the flow rate of liquid through the coupon, cross-sectional area, and the length of diffusion were calculated. The head of liquid was taken as the average head of liquid on the coupon (about 6.35 cm).

The experimental permeabililty coefficients (K), determined for the 1/4 inch coupons, are given in Table 8. The literature review indicated that the permeability coefficient for water ranges from 3×10^{-11} cm/sec to 3×10^{-6} cm/sec[5]. The experimental values for the aqueous solutions shown in Table 8 fall within this range, although towards the upper limit.

TABLE 8. EXPERIMENTAL PERMEABILITY COEFFICIENTS CALCULATED FROM CONSTANT CONTACT EXPERIMENTS

Solution	Porosity (%)	$Qx10^4$(a) (cm/s)	$Kx10^7$(b) (cm/s)
Water	High (17.8)	3.33	4.11
	Low (11.6)	3.24	4.00
40% DMSO-Water	High (17.4)	4.51	5.56
	Low (11.6)	0.556	0.68
50% Acetone-Water	High (17.9)	7.97	9.83
	Low (11.6)	3.694	4.56
FREON 113•	High (17.1)	20.25	25.96
	Low (11.6)	10.44	12.87
50% MEA-Water	High (16.8)	6.82	8.41
	Low (11.6)	1.812	2.235

(a) Q = flow rate through coupon

(b) K = permeability coefficient

6.3 Constant Contact Application Conclusions

Results from the constant contact experiments indicate that:

- Application of a liquid decontaminant to porous materials by the use of gels or foams does not appear as preferable as a spray application because of mass transfer limitations created by displacement of air within the pore matrix by the liquio decontaminant;
- decontamination of concrete sumps by the constant contact method will be enhanced by the use of agitation.

Further efforts on the constant contact method are not required.

7.0 EVAPORATION EXPERIMENTS

Facility decontamination involving a liquid based decontaminant must consider the evaporation rate of the liquid from concrete following the treatment. It is necessary to determine whether or not supplemental procedures are required during decontamination (e.g., ventilation or a secondary treatment to remove the excess decontaminant).

7.1 Description of Evaporation Experiments

The evaporation rate was determined as follows. The evaporation tests were carried out by simulating single surface evaporation such as would be present when treating concrete walls and floors in the field. To further simulate in-field application, the coupons used in the tests were ones that had previously been used in the spraying experiments.

The procedure used is as follows:

- Record weight of sprayed coupon
- Place coupon, sprayed side up, on a neoprene rubber sheet and record time

- Record weight and time at intervals between one hour and one day*
- Stop experiment when coupon is near original weight.

7.2 Discussion of Evaporation Results

Evaporation rates were obtained for 40 percent DMSO/water, 50 percent acetone/water, FREON 113, and 50 percent MEA water. Both low and high porosity mortar coupons were used in the tests. Figures 26 and 27 show the weight loss due to evaporation for low and high porosity coupons, respectively. In these figures, ΔW represents a normalized weight given by the expression:

$$\Delta W = \left(W_t - W_o\right) / \left(W_{SAT} - W_o\right)$$

where W_t = weight of coupon at each weighing period
W_o = dry weight of the coupon
W_{SAT} = saturated weight of the coupon

The curves indicate that the evaporation rate of all of the aqueous solutions was low enough such that evaporation will have little effect on the application of liquid by the spraying method. FREON 113, however, evaporated rapidly from the coupon. The high evaporation rate was confirmed in the spraying experiments involving FREON 113. In these experiments, the coupons achieved substantially no weight gain from absorption of the FREON 113 even after repeated sprayings. Thus, in depth decontamination of concrete by the spray application does not appear feasible. It may become feasible if a high vapor partial pressure of FREON 113 is maintained in the building being decontaminated. This would necessitate the use of either remotely operated sprayers or self-contained breathing apparatuses; both of which are disadvantages.

* The interval depended on the solution tested.

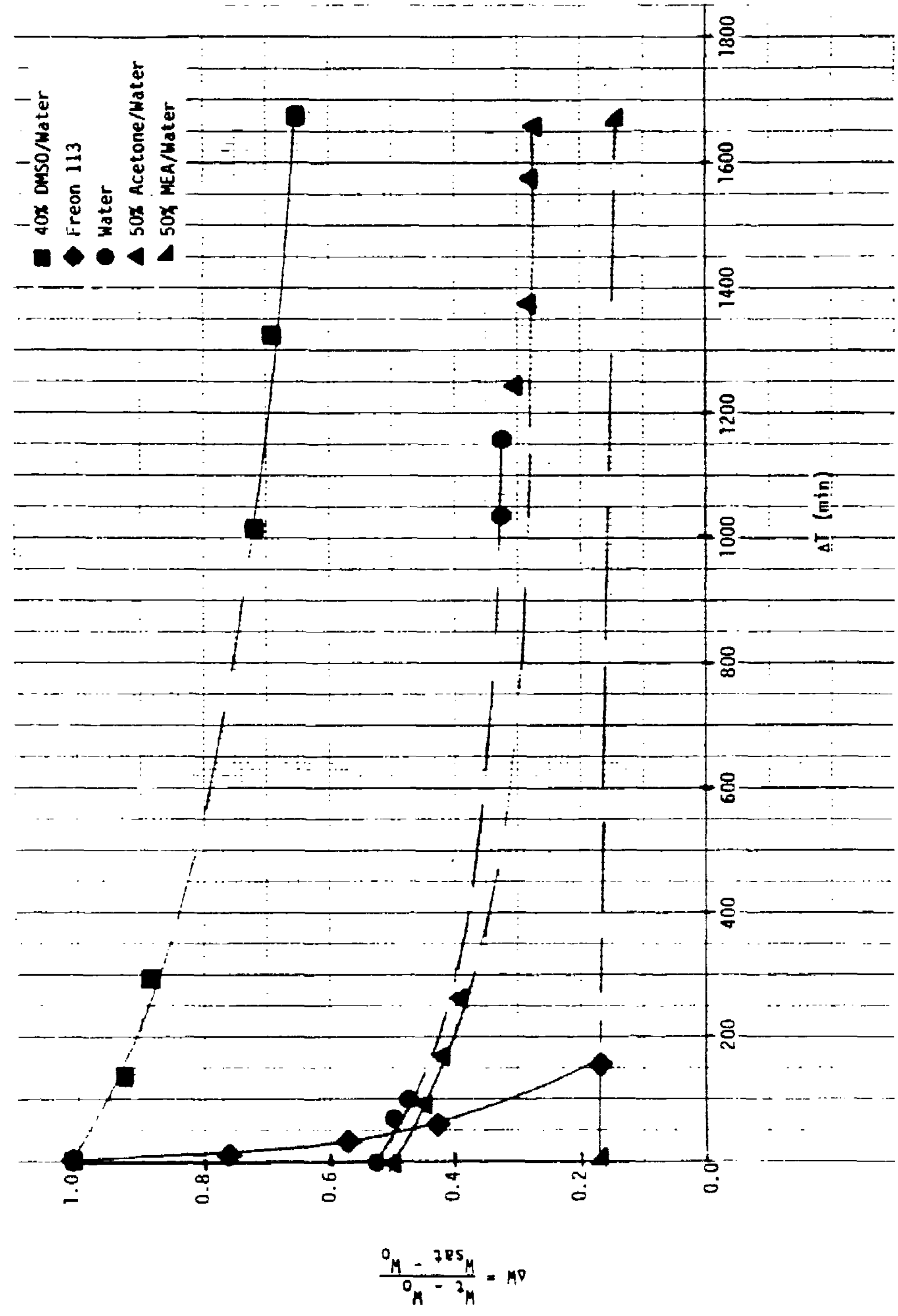

FIGURE 26. EVAPORATION RATES (LOW POROSITY COUPONS)

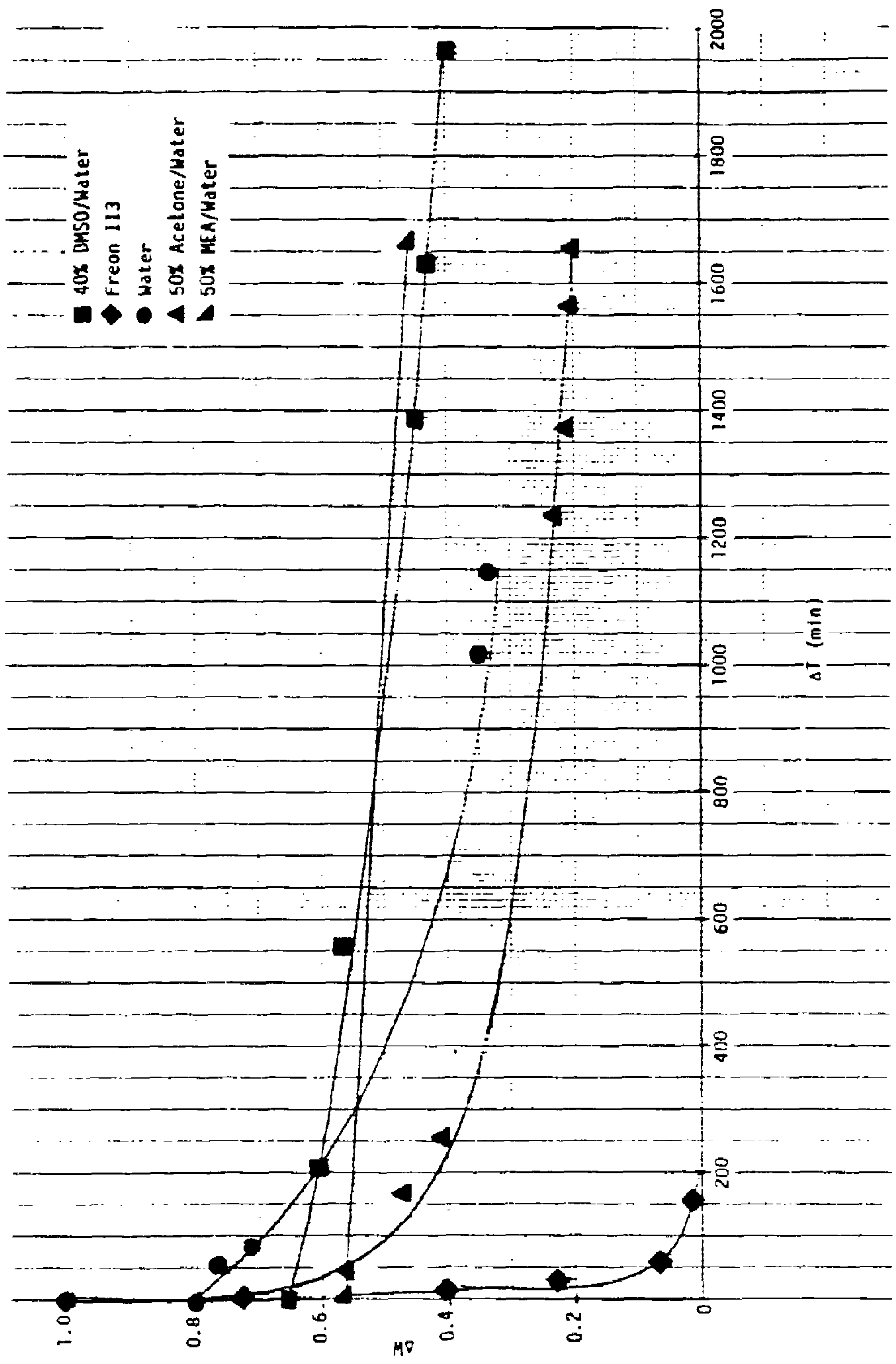

FIGURE 27. EVAPORATION RATES (HIGH POROSITY COUPONS)

After decontamination is complete, it appears that the evaporation rate of most aqueous based decontaminants is sufficiently rapid such that supplemental procedures to remove the decontaminant may not be required.

8.0 CONCLUSIONS/RECOMMENDATIONS

General conclusions drawn from an analysis of the experimental data obtained during this study are as follows:

- The application of liquid decontaminants to concrete by spraying appears feasible if the depth of penetration of the contaminant does not exceed 1/2 to 1 inch;
- sufficient experimental data was generated such that liquid and recycle requirements, application times, and preliminary equipment requirements necessary for an economic analysis can be determined;
- application times and steady-state rates for the constant-contact method were obtained;
- The penetration rate is not increased by maintaining a standing liquid decontaminant on a porous surface as compared with periodic spraying of the same decontaminant.
- application times for decontamination of CW agent-contaminated concrete structure with ammonia gas were determined;
- preliminary experimental data was generated to aid specification of Phase III pilot scale starting conditions for the most promising chemical decontamination concepts if an aqueous solution is selected from Phase II studies;
- experience gained on the application of candidate decontaminants to mortar will facilitate analysis

of subsequent mortar coupon decontamination experiments in both Tasks 3 and 4 as well as future field experiments.

8.1 Extension of Results to Field Decontamination

The primary concern in extending the experimental results obtained in this subtask to field decontamination efforts is the representativeness of mortar coupons used in this study in relation to real world concrete structures. Factors which must be considered to determine this relationship include 1) the coupon porosity, 2) the presence of aggregates and 3) the chemical composition. These factors are discussed as follows.

Coupons of both a high and a low porosity were selected for experimental evaluation. The porosities were selected to be within the range of reported values for commercial concrete. The high porosity was near the upper range of reported values and the low porosity was near the lower range. Analysis of the experimental data indicates that similar results (i.e., trends in the data) were observed for coupons of the two different porosities evaluated under the same set of conditions. The only apparent difference between the results obtained for each of the two porosity levels is that penetration rates increased and penetration times decreased when the porosity increased. Also, data was generated to determine the magnitude of this effect of porosity on liquid and gas penetration. Thus, based on the experimental data and the use of coupon porosities which are within the range of commercial values, it appears that extension of the results to field concrete structures can be performed in so far as the porosity is concerned.

A primary difference between the coupons used in this subtask and commercial concrete is the lack of aggregate in the mortar coupons. Aggregate, typically used to add bulk and strength to mortar, was not used in the coupons because of size limitations discussed in Section 3.1. Factors which must be considered when determining the effect of the presence of aggregate on the results obtained with mortar coupons include:

- Typical aggregate (e.g., granite) is relatively impermeable (to both contaminent and decontaminent);
- limestone aggregate (less typical) has a porosity similar to the mortar used in the experiments,
- aggregate pores which form between the aggregate and cement matrix are of comparable size to air pores in mortar (see Appendix A).

Thus, although the presence of aggregates may affect the overall porosity of the material, it is anticipated that similar trends will be observed in field tests on commercial concrete as were observed in the laboratory tests with mortar.

The chemical composition and method used to prepare the coupons was similar to that of commercial mortar. Commercial grade sand, cement and water were used and established mortar preparation, casting and curing procedures were followed as closely as possible. Although the exact chemical composition and preparation method can vary from site to site, it is anticipated that the effect of composition on the trends observed in this study will be nominal.

Thus, the mortar coupons used in this experimental study appear representative of commercial concrete and, as such, similar trends should be observed when field concrete decontamination tests are performed.

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2) Wakao, N. and Smith, J.M., Chem. Eng. Sci. 17, 825-34 (1962)
3) Gummerson, R.J., Hall, C., Coff, W.D. Building and Environment 15, 101-108, (1980).
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APPENDIX A

CONCRETE PROPERTIES

APPENDIX A

CONCRETE PROPERTIES*

The ability of a porous material such as concrete to be penetrated by a chemical decontaminant is related to the material properties of the concrete, including the porosity and the pore matrix. The pore matrix (i.e., pore size distribution and pore type) will determine the physical method by which the chemical decontaminant penetrates concrete (e.g., Knudsen gas diffusion versus bulk gas diffusion). The porosity (i.e., volume fraction of voids) is a determining factor of the rate by which the chemical decontaminants penetrate into concrete. More rapid penetration by the chemical occurs as the porosity of concrete increases. Because the porosity of commercial concrete can vary from about 5 to 20 volume percent, a wide range of penetration rates is possible for a given decontaminant.

Concrete consists of aggregate, cement and water. Aggregate can be further classified as fine particles less than one-quarter inch and coarse particles larger than one-quarter inch. Aggregate, the inert portion of concrete, is generally impermeable. Its primary contribution is to add bulk and strength to concrete. In contrast to aggregate, the cement and water affect the porosity and ultimate pore matrix of concrete. The mechanism by which the cement and water affect the porosity of concrete can be determined by analyzing the concrete preparation process as follows.

When concrete is poured, it consists of aggregate, cement, water and entrained air. During curing, the cement reacts with water to form a hydrated gel. As the gel forms, it expands and fills the voids created from reaction of the water. Because the hydrated gel has a larger bulk volume than the unhydrated cement and the water, essentially all of the bulk volume can be filled with the hydration products when the water to cement (W/C) ratio is favorable (i.e., about a 0.4 W/C ratio). When the water to cement ratio is

* From "Significance of Tests and Properties of Concrete and Concrete Aggregates", ASTM Special Technical Publication No. 169, 1956.

high, all of the water does not react and, as such, the bulk volume is incompletely filled by the hydrated gel. The remaining water is readily evaporated from the interconnected pores at relative humidities below about 40 percent.

The interconnected pores formed by evaporation of excess water are termed capillary pores. The hydration gel, which expands into the capillary pores, is also capable of holding evaporable water. This water, when evaporated, leaves pores termed as gel pores. The gel pores constitute approximately 25 percent of the bulk volume of the hydration products. As the W/C ratio decreases, the volume of gel pores increases while the volume of capillary pores decreases.

Another factor which contributes to increasing the formation of gel pores while decreasing the amount of capillary pores is the curing time. As curing time increases more gel pores are formed. The gel pores, which interconnect the capillary pores, restrict the movement of water because of their smaller size. As such, water is retained longer allowing an increase in the time to react. Restricted movement of water is illustrated by reports that drying time increases with an increase in cure time*.

The remaining types of pores include air voids and aggregate pores. Air voids are caused by air entrained in the initial poured mixture. Aggregate pores are formed by voids formed between the hydrated gel and the aggregate.

A summary of the various pore types follows:

- Capillary pores - 5×10^{-5} to 5×10^{-4} inches in diameter (1 to 10 μm) - a total of 1 to 5 percent of total volume of concrete
- Gel pores - about 10^{-6} inch (about 0.01 μm) - a total of about 4 to 8 percent of total volume of concrete
- Air voids - about 5×10^{-7} to 0.1 inch (about 0.01 to 2500 μm) - a total of about one to 10 percent of total volume of concrete.
- Aggregate pores - about 5×10^{-4} to 5×10^{-2} inches (10 to 1000 μm).

* Hughes, B.P., Lowe, I.R.G. and Walker, J. Brit. J. Appl. Phys. 17, 1545-52 (1962).

APPENDIX B

COUPON PREPARATION

APPENDIX B

COUPON PREPARATION

The spraying, diffusion and constant contact experiments utilized 5 inch by 5 inch test coupons composed of a mixture of water, cement and sand (i.e. mortar). Both low porosity and high porosity mortar coupons were prepared in order to more closely simulate the variety of concretes which can be found in the field. Three coupon thicknesses (1/4 inch, 1/2 inch and 1 inch) were fabricated of each the low porosity and high porosity mortar. The thicknesses were specified to allow acquisition of data in a realistic time frame and to allow the effect of mortar thickness on the application method to be determined.

The preparation method for the mortar coupons considered the type of mold used to cast the coupons, the formulation of the mortar mixture, and the curing procedure.

B.1 Mold Type

The casting molds were specified with the following considerations:

- A mold with a very smooth surface was required to which the cast coupons would not adhere. The use of a parting compound such as oil was not used because of probable contamination of the coupon surface. As such, the molds were made from PLEXIGLAS.
- Reusable molds were required because of the requirement of a large quantity of coupons for the tested (over 100). PLEXIGLAS molds fulfilled this requirement.
- Warpage of the coupon was minimized by casting the coupons in a vertical orientation.

The molds, shown in Figure B-1, were assembled by the following procedure. Each divider was stood on end and the spacers were placed in such a way that the holes through the dividers and spacers lined up. The bolts were

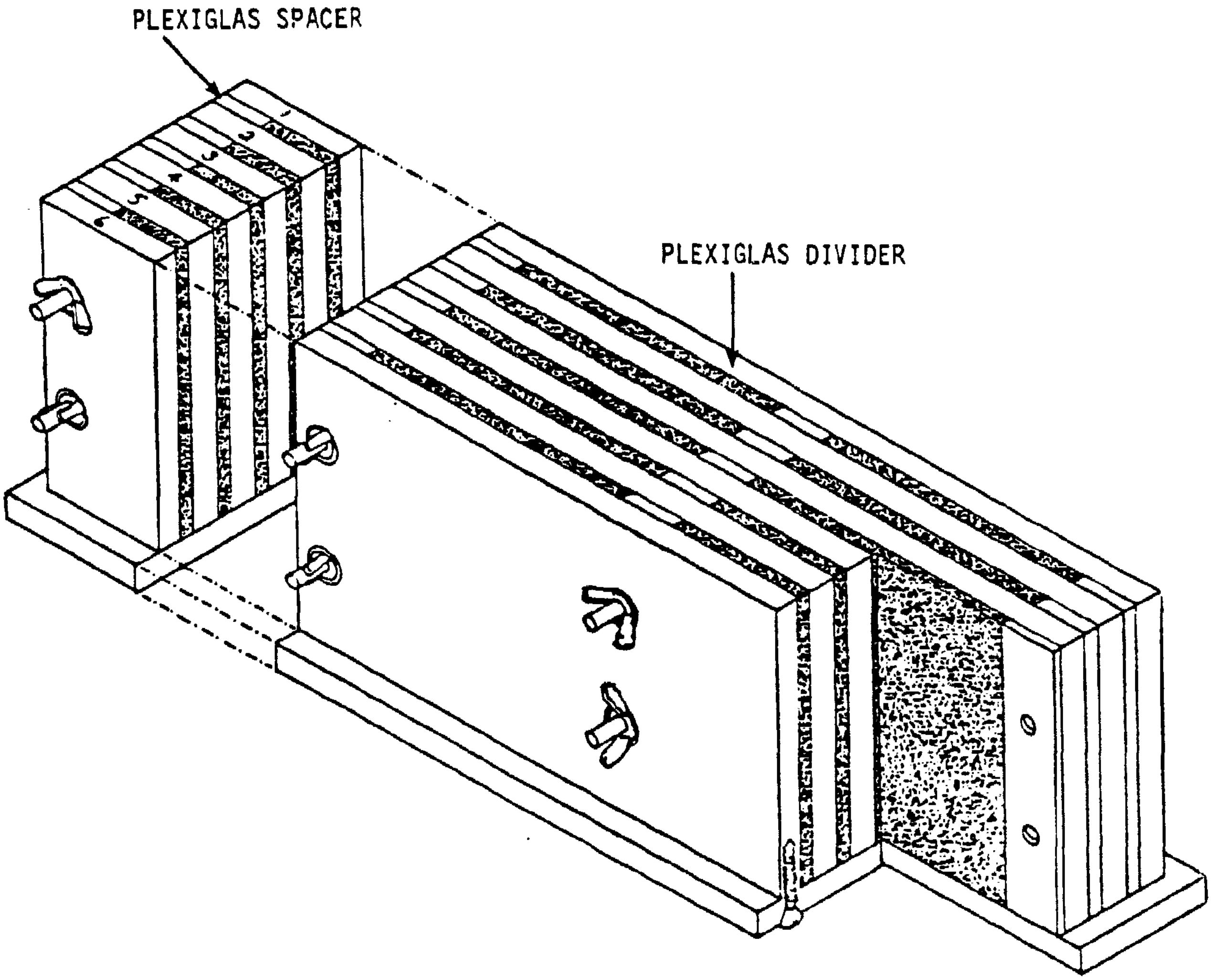

FIGURE B-1. MOLD USED TO CAST MORTAR COUPONS

inserted and the wing nuts were tightened so contact was made with the dividers. Five dummy coupons were inserted along the first row of spacers and the adjacent bolts tightened. This process was repeated until there was a 5-inch gap between each spacer. The bottom piece was then attached by tightening the six screws into pretapped holes in the dividers on the ends (three holes in each divider). Modeling clay was then placed in the crack between the bottom piece and the dividers to prevent water from leaking from the bottom of the mold.

After the molds were completely assembled, lines were drawn using a permanent ink marker on the top edge of the mold through the dividers and spacers. These lines were used to ensure each piece could be placed in its original position after the molds were taken apart.

B.2 Mortar Mixture

Concrete is composed of a mixture of mortar (water, cement and sand) and aggregate. The ratios of each of these components is dependent on the desired consistency and quality of the concrete as well as the quality of the ingredients. It is important to note that the quality of the cement, sand and aggregate varies from location to location.

The standard procedure used to specify the ratio of components in concrete is to first determine the desired quality of the concrete, for example 2500 pound concrete, 3000 pound concrete, etc. The quality along with the unique properties of the aggregate, sand and cement, fix the aggregate to sand to cement ratio. Water is added to the mixture to obtain the desired workability (related to the ultimate use of the concrete). In this study, deviations from this standard procedure were made by first specifying the water to cement ratio and then specifying the amount of sand added. The reasons for these deviations are as follows.

It was anticipated that the porosity of the coupon would affect the results of the application methods (i.e., spraying, NH_3 diffusion, and constant contact). Because the porosity of concrete used in the field can vary substantially, both high porosity and low porosity coupons were prepared. The exposure of coupons of different porosities to identical test

conditions would allow the effect of porosity on the application method to be determined. As such, the feasibility of the method as applied to a wide range of concrete types can be established.

The water to cement (W/C) ratio has been shown to have the greatest effect on determining the porosity of concrete. Two W/C ratios were selected - 1) a 0.4 W/C for a low porosity material and 2) a 0.6 W/C for a high porosity material. Once the W/C ratio was fixed the proportion of sand was determined experimentally by preparation of trial batches. The proportion of sand determined the workability of the mixture and subsequent properties of the coupon. If the cement to sand ratio is too high the mixture will be too wet and segregation will occur. If the cement to sand ratio is too low the mixture will be too dry and the sample will have an excess of air voids. The water to cement to sand ratio for the low porosity mortar was determined to be 0.4:1 :1.6 respectively, and for the higher porosity mortar was 0.6:1:3, respectively.

No aggregate was used in the coupons. This should not affect the representativeness of the coupon in relation to commercial concrete because aggregate is typically either impermeable or as permeable as the mortar (mixture of cement, water and sand). Moreover, when casting concrete, the largest size particle must be less than one-third the size of the smallest dimension of the mold. If aggregates larger than this are used, the aggregate particles will clump together resulting in the formation of large voids in the mold. The smallest dimension of the coupons is 1/4 inch. Thus, aggregate of (1/4) x (1/3) = 1/12 inch should be used (equivalent to sand).

The procedure used to prepare the mortar coupons was as follows. Each high porosity batch contained the following:

- 750 grams water - tap water
- 1250 grams cement - Portland Type I
- 3750 grams sand - minus 10 sieve size fraction, Fidley -400 concrete sand

Each low porosity batch contained the following:

- 700 grams water
- 1750 grams cement
- 2800 grams sand

The mixing procedure was as follows:

- Water, sand, and cement were weighed to the nearest gram.
- The water was poured in a mixing bowl.
- The cement was added and was immersed in the water.
- The mixture was allowed to stand for one minute to allow the water to wet the cement.
- The mixture was mixed on low speed for one-half minute (Hobart Model A-120 mixer).
- The sand was added over a period one-half minute, while leaving the mixer on.
- Mixing was continued for one-half minute.
- The mixer was turned off and the mixture was allowed to stand for one and a half minutes.
- The mixture was then mixed on medium speed for one and a half minutes.

At this point, the mortar was ready to be cast in the mold. The mixing paddle was removed and the mortar was quickly poured into the molds located on a laboratory vibrating table. The vibration of the table assured that all the cavities of the mold were completely filled. When the mold was filled, the table was turned off and the excess mortar was scraped off the top of the mold ensuring the tops of the coupon were not disturbed. The vibrating table was turned back on for approximately 10 seconds and to completely fill all the cavities in the mold. Overflow mortar was wiped from the sides of the mold with a damp cloth and the mold was loosely covered with aluminum foil. The entire mold was then placed in a fog room

(72 F, 100 percent relative humidity. After 24 hours in the fog room, the mold was removed and disassembled. The individual coupons were then placed back in the fog room to cure. The coupons were laid flat on screens in the fog room to allow exposure of most of the surfaces to 100 percent relative humidity.

B.3 Curing

Curing is the reaction of cement with water to form a hydrated gel. The recommended curing period is 28 days; however, due to time limitations and because properties of mortar (e.g. porosity) do not substantially change after a 14 cure, a 14 day cure was used for most of the coupons.

After curing, the coupons were removed from the fog room and all excess moisture was removed from the coupon surfaces by wiping with a damp cloth. Each coupon was numbered, weighed and placed in a constant temperature/humidity room (72 F and 50 percent $\pm$ 2 percent relative humidity) for equilibriation. The coupons were stood on their edge in the room to expose the most surface area possible. Every two days, the weights of the even-numbered coupons were recorded. When the weight loss was less than 0.1 g, the coupons were considered dry and ready for use. Typically, 5 to 7 days were required to reach a constant weight.

APPENDIX C

POROSITY TEST METHODS

APPENDIX C

POROSITY TEST METHODS

The procedure used to perform the porosity tests was taken from ASTM Method C 642, "Standard Test Method for Specific Gravity, Absorption, and Voids in Hardened Concrete". Three measurements are required to determine the percent voids (i.e., porosity) in concrete:

- Oven-Dry Weight (A) - Oven-dry for 24 hours at 212-230 F.
- Immersed Weight (B) - Weigh suspended in water after boiling and cooling submersed in water.
- Saturated Weight After Boiling (C) - boil submersed specimen for five hours, allow to cool to room temperature, remove surface moisture, and weigh in air.

These three weights are used to determine percent volume of permeable pore space (void percent) by the following equation

$$\text{Void, \%} = \frac{(C-A)}{(C-B)} \times 100$$

This ASTM procedure was designed for concrete cylinders, cores, or beams which weigh over 800 grams. Since the samples used in this Subtask were smaller and had a geometry of a rectangular solid with a much higher surface-to-volume ratio, it was believed that boiling for a period less than five hours would suffice. This was tested by boiling three samples for two hours, cooling, wiping residual surface moisture, weighing and taking an immersed weight. Then, the same three samples were reboiled for five hours, allowed to cool, surface moisture wiped off, the coupon weighed and an immersed weight taken. The average difference between the immersed weights of the same coupon was 0.08 percent and the average difference between the saturated weights of the same coupon was 0.08 percent. Based on these results, the porosity tests were conducted by boiling coupons for two hours. It was also felt that taking

an oven-dried weight was not necessary because an oven-dry weight would give the total void space of a coupon which is completely dry and not typical of what would be found in field applications. Since a value for the voids available for moisture penetration in a sample equilibrated to ambient humidity was more typical of this program's needs, the oven-dry weight was replaced with the equilibrium weight.

The modified ASTM procedure is as follows:

- Record equilibrium weight (A)
- Boil submersed coupons for two hours and allow to cool to room temperature while submersed - about 72-77 F
- Suspend in water and record immersed weight (B)
- Surface-dry boiled samples with damp towel and record saturated weight (C).

Use following ASTM equation as a measure of porosity.

$$\text{Percent Voids} = \frac{C-A}{C-B} \times 100\ \%$$

APPENDIX D

CONSTANT CONTACT DATA

APPENDIX D

CONSTANT CONTACT DATA

Results from constant contact experiments involving 1/2 and 1 inch, low and high porosity coupons are shown in Figures D-1 through D-4. Constant contact data are shown in the following pages.

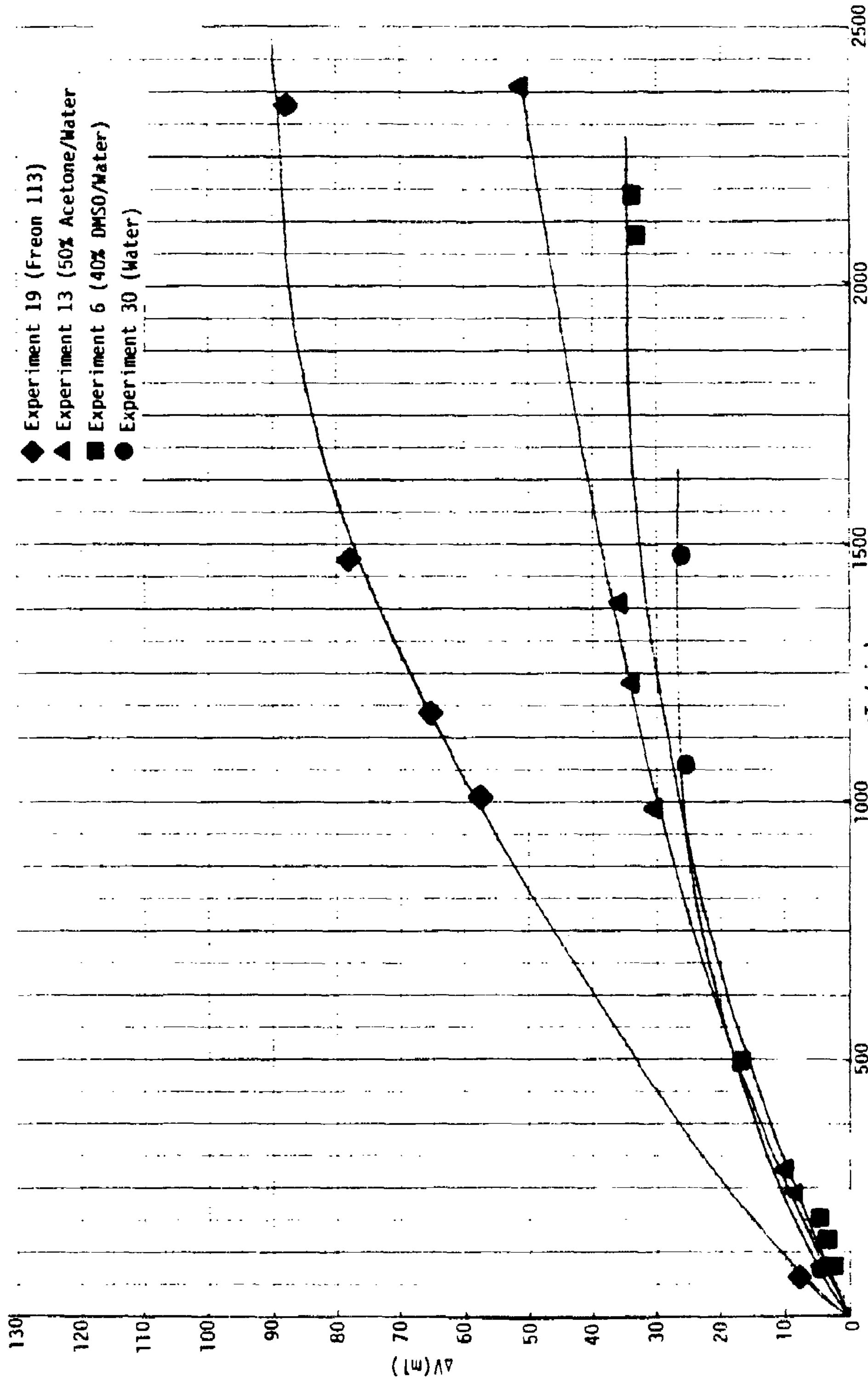

FIGURE D-1. CONSTANT CONTACT TEST RESULTS (1/2-INCH LOW POROSITY COUPONS)

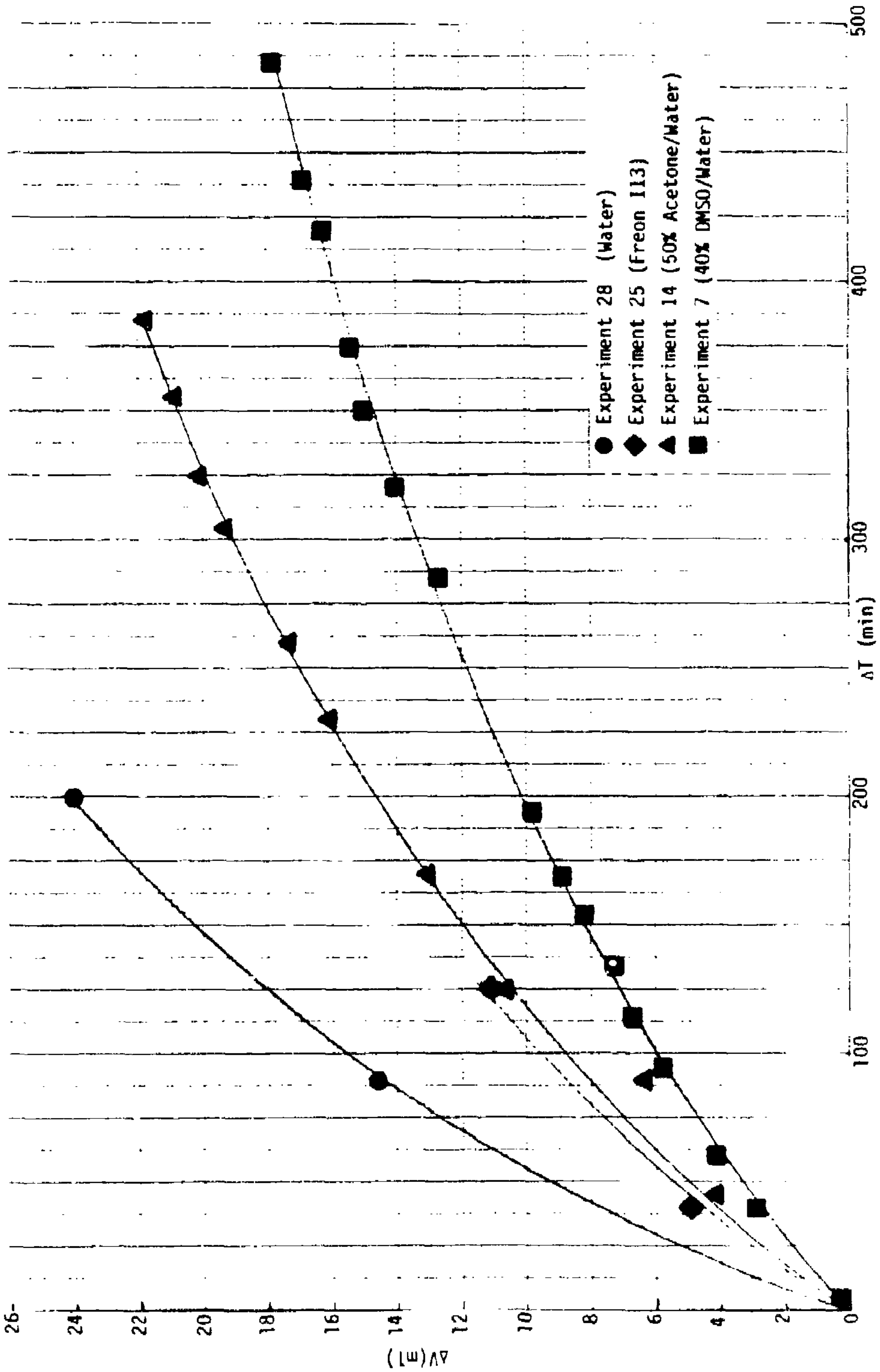

FIGURE D-2. CONSTANT CONTACT RESULTS (1/2-INCH HIGH POROSITY COUPONS)

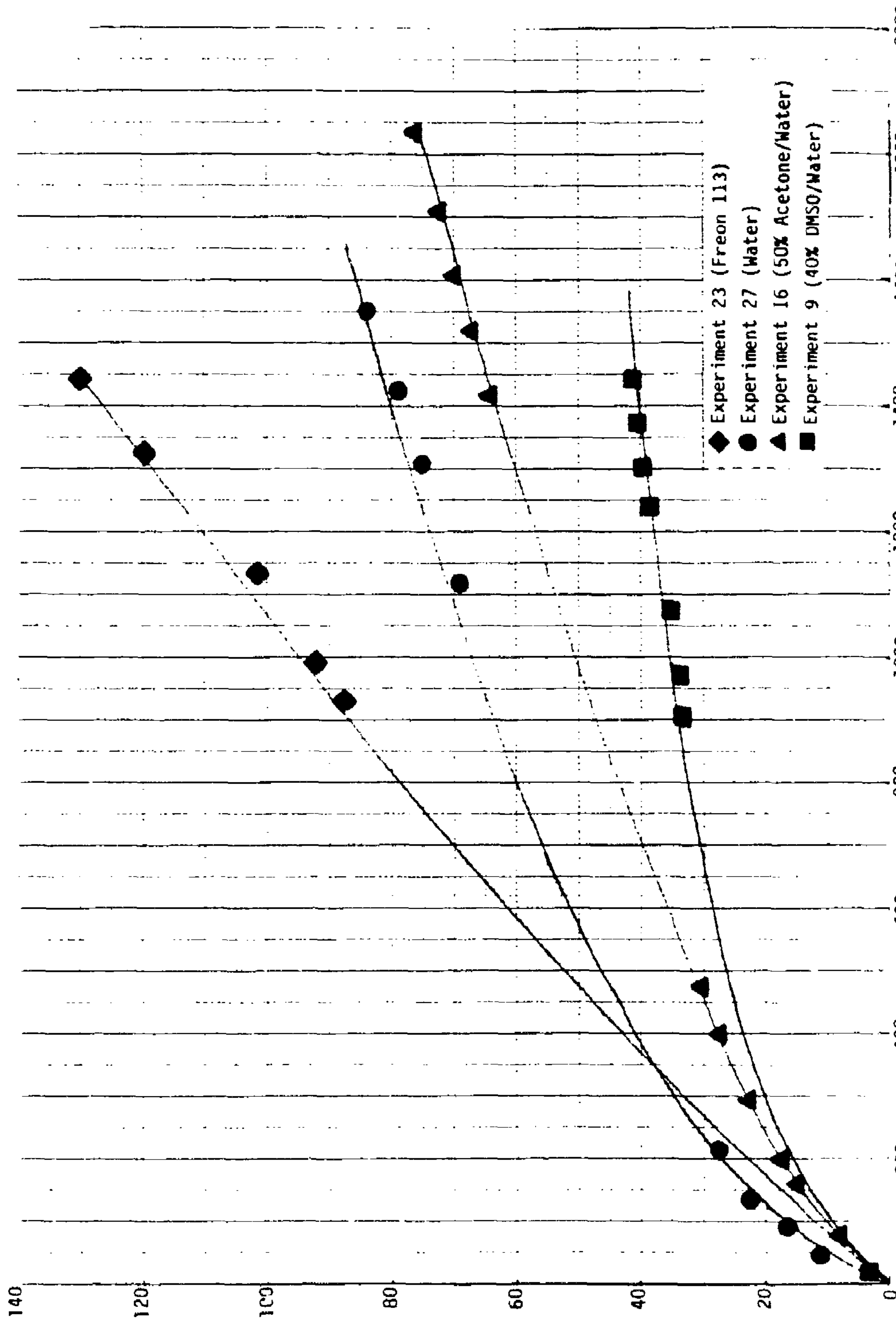

FIGURE D-3. CONSTANT CONTACT TEST RESULTS (1-INCH, HIGH POROSITY COUPONS)

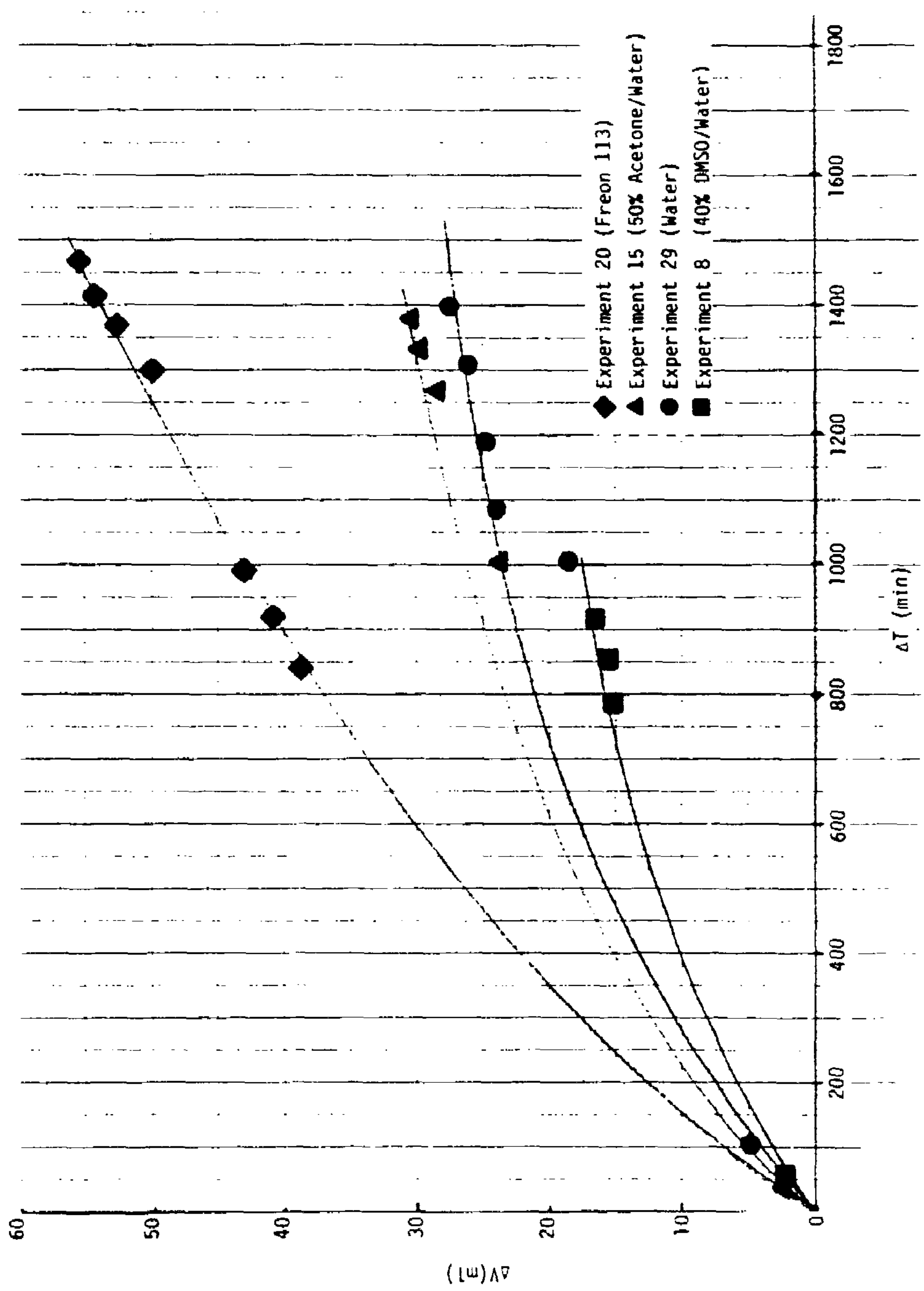

FIGURE D-4. CONSTANT CONTACT TEST RESULTS (1-INCH LOW POROSITY COUPONS)

APPENDIX IV

SUBTASK 5. STAINLESS STEEL SURFACE DECONTAMINATION SCREENING

TEST REPORT

FOR

TASK 3 SUBTASK 5

STAINLESS STEEL SURFACE
DECONTAMINATION SCREENING

to

UNITED STATES ARMY
TOXIC AND HAZARDOUS MATERIALS AGENCY

by

E.R. Zamejc
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EXECUTIVE SUMMARY

Five decontamination concepts (Steam, OPAB, Hot Gases, Vapor Circulation, and Flashflasting) were evaluated for their decontamination effectiveness of agent contaminated stainless steel surfaces. The results indicate that Steam, Hot Gases and OPAB are the most promising concepts for further study. The Steam and Hot Gases concepts decontaminated stainless steel contaminated with HD, GB or VX to below the detectable limit. The OPAB concept decontaminated stainless steel to below the detectable limit when GB was the contaminant. Results suggest that a similar decontamination effectiveness can be achieved with OPAB when either HD or VX is the contaminant. As such, BCL suggest that the Steam, OPAB and Hot Gases concepts be further evaluated in the subsequent subtask (Subtask 6) for decontamination effectiveness of painted mild steel, unpainted mild steel and painted stainless steel matrices. The decontamination of concrete will be a subject of a separate subtask.

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FOR
STAINLESS STEEL SURFACE DECONTAMINATION SCREENING
CONTRACT DAAK11-81-C-0101
to
UNITED STATES ARMY
TOXIC AND HAZARDOUS MATERIALS AGENCY

1.0 INTRODUCTION

The development of novel concepts for the decontamination of chemical agent-contaminated buildings is being carried out by Battelle Columbus Laboratories (BCL) for the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) under Contract No. DAAK11-81-C-0101. In the previous phase (Task 1), ideas were systematically developed into concepts for decontaminating buildings and equipment. These concepts were evaluated and ranked with respect to technical and economic factors. Also, knowledge gaps relating to application of the most promising concepts were identified. These knowledge gaps are being addressed through laboratory evaluation of the concepts in Task 3.

2.0 OBJECTIVE

The objective of this subtask was to provide preliminary evaluation of five concepts for their decontamination effectiveness using stainless steel contaminated with HD, GB, or VX as the test substrate. The concepts evaluated in this subtask included:

- Hot Gases
- Vapor circulation/RADKLEEN®
- Steam

- OPAB (aqueous solution of 1-octylpyridinium 4-aldoxime bromide)
- Flashblast.

Results of Subtask 5 experiments are to be used to (1) select three of the most promising concepts (i.e., those concepts which effectively decontaminated the coupon) for further evaluation later in Subtask 6, and (2) provide a basis for selection of operating parameters for decontamination of other substrates (e.g., painted stainless steel, painted mild steel, unpainted mild steel and concrete in Subtask 6, Steel/Concrete Tests.

3.0 APPROACH

In the tests, stainless steel coupons were spiked with a known quantity of agent (HD, GB, or VX) and the decontamination* treatment applied. Following the treatment, the coupons and the samples accumulated during the experiment were analyzed for residual agent. The primary criterion used to determine the effectiveness of the decontamination treatment was the amount of residual agent remaining on the coupons following decontamination. A treatment was considered effective if the coupons were decontaminated to below the detectable limit. The treatment was also considered effective if nearly complete decontamination was achieved and trends in the data suggested that decontamination to below the detectable limit can be reasonably achieved by modification of the conditions used to apply the decontaminant.

Another factor of equal importance to decontamination efficiency was whether or not the gaseous and/or liquid effluents from the decontamination tretment contained undecomposed agent. Application of the concepts to field decontamination will require identification of those effluent streams which contain undecomposed agent such that a supplemental treatment to remove/decompose the agent can be specified. It is important to note that qualitative rather than quantitative information confirming the presence of undecomposed agent in the effluents is sufficient to determine the

* Decontamination of the coupon implies either agent destruction and/or physical removal of undecomposed agent.

need for a supplemental treatment. It was judged that additional costs required to design an experimental system which quantitatively collects traps agent from the effluent streams were not justified. As such agent material balances were not performed.

A description of the test chamber, collection system and analytical procedures follows.

3.1 Test Chamber Description

In order to safely implement the decontamination concepts, a test chamber was prepared which met the following design criteria:

- Sized to fit within a laboratory hood
- Constructed to contain all toxic and hazardous vapors that might be released from the sample coupons
- Samples must be exposed to the decontamination environments in a manner closely simulating field conditions
- Provisions made for the application of vapor decontaminants (hot gas, steam, FREON® 113 vapor), a liquid decontaminant (OPAB solution) and the flash-blast device
- Capabilities must be provided to permit qualitative collection and sampling of all gaseous and liquid effluents
- The need for frequent change of samples, decontamination, and general cleanup requires easy access to the interior of the chamber.

As shown in Figure 1, the test chamber was designed and fabricated as a multi-compartment box of roughly rectangular geometry. It consisted of an exposure chamber, a collection chamber, and a coupon holder. Also associated with the chamber was a hot gas delivery system, a FREON vapor/steam delivery system, and an OPAB solution delivery system. The entire chamber was insulated with 4 inches of Cera® wool insulation to minimize heat losses when operating at temperatures above ambient. The major components of these

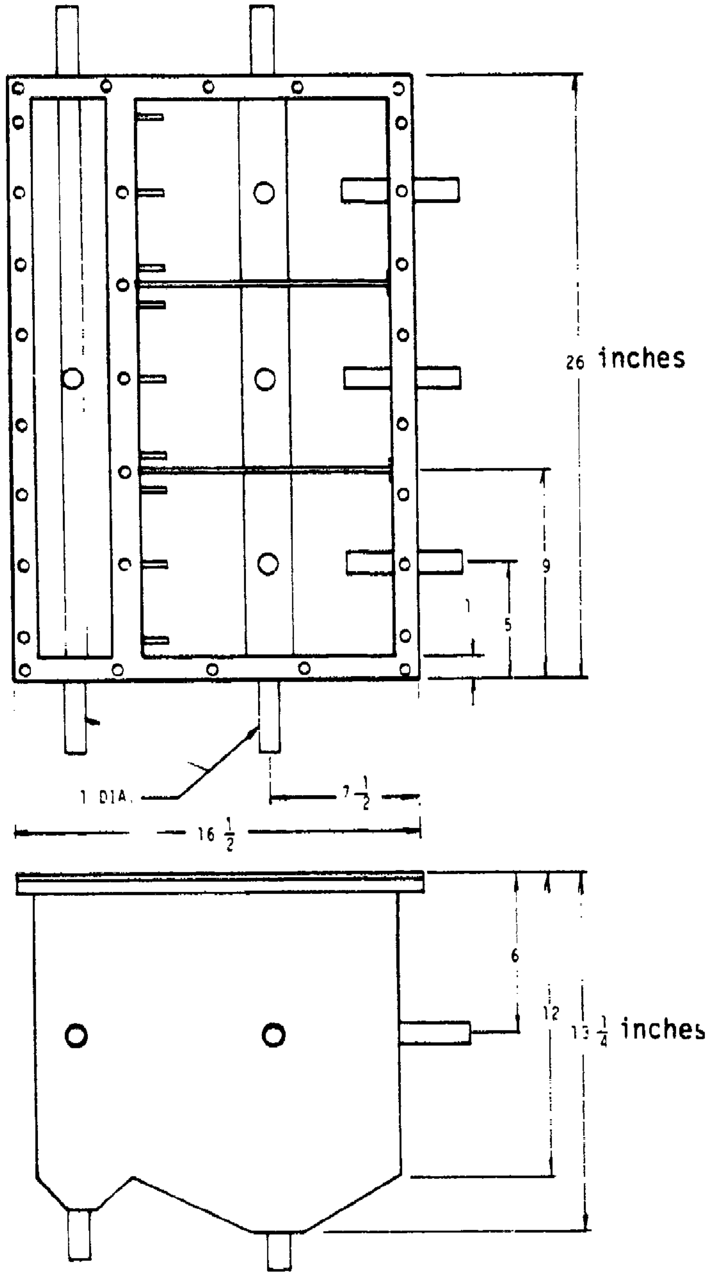

FIGURE 1. TEST CHAMBER DIMENSIONS

systems were constructed of 304 stainless steel. Gasket materials were selected for thermal stability and/or resistance to solvent attack (i.e., compressed asbestos, neoprene, Viton® and Teflon®).

The as-built test chamber is illustrated in Figures 2 and 3. A brief description of the major components of the test chamber (i.e., exposure chamber, collection chamber and coupon holder) is as follows.

3.1.1 Exposure Chamber

The purpose of the exposure chamber was to provide containment of the atmosphere to which the sample coupons are being exposed while simultaneously allowing collection of the liquid and gaseous effluents. The shell of this 2½-cubic foot chamber was constructed of 16-gauge stainless steel sheet supported and reinforced with 1/4 x 1-1/2 x 1-1/2-inch angle iron. All joints and seams were welded except the top, which was sealed with Gore-Tex® flexible (Teflon) gasket. The top was removable for easy access.

Two inserts were provided in the exposure chamber such that removable partitions could be installed. The partitions*, when in place, would divide the exposure chamber into three identical compartments. While these compartments would not be completely sealed from each other, they would nonetheless permit simultaneous exposure of three replicate coupons to identical but independent reaction conditions. The bottom of each compartment were designed to permit collection of independent samples of the liquids draining from each compartment (sump). For Subtask 5 experiments, the sumps were connected to one common sump line external to the exposure chamber.

The exposure chamber was separated from the collection chamber by a wall containing three 6-inch square openings, one opening centered in each of the compartments. The wall was fabricated with 1/4-inch thick stainless steel to provide the strength necessary to support the coupon holders. Bolts, welded to the chamber adjacent to these openings, were provided for mounting coupon holders.

Three 1/2-inch pipe nipples were welded onto the front wall of the exposure chamber, one centered in each of the compartments and aligned with

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* Partitions were not employed in Subtask 5 tests.

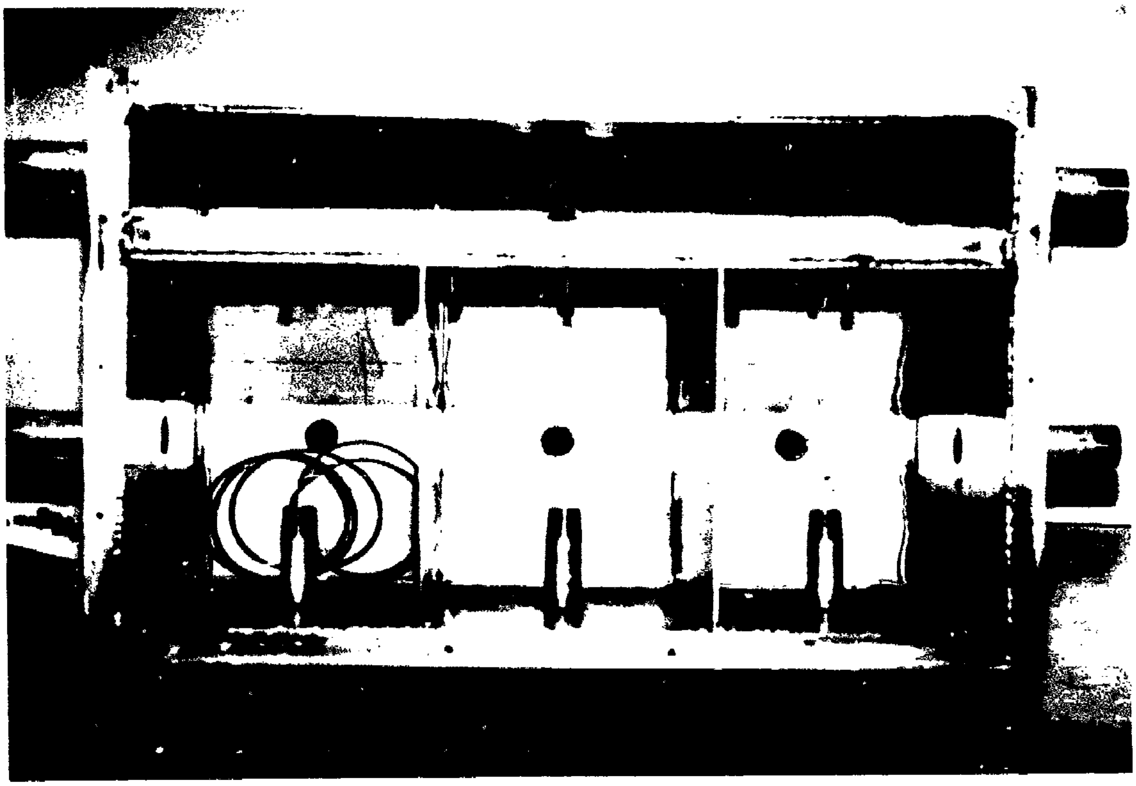

FIGURE 2. TOP VIEW OF DECONTAMINATION TEST CHAMBER SHOWING INTERNAL CONFIGURATION

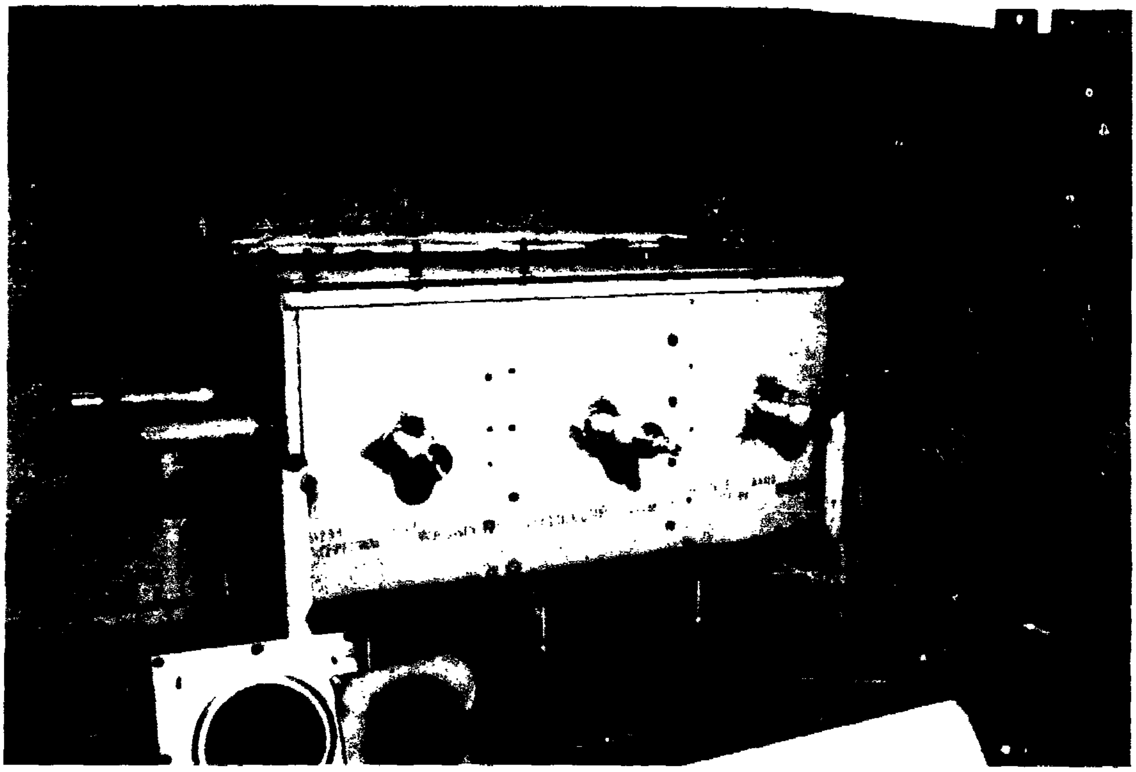

FIGURE 3. FRONT VIEW OF DECONTAMINATION TEST CHAMBER

the center of the sample coupon holders. These fittings provided entry for spray nozzles (OPAB concept) and for electrical leads (Flashblast concept).

Entry for gases/vapors (Hot Gases, Steam and Vapor Circulation concepts) was provided through a 1-inch pipe nipple welded to and located in the center of one side of the chamber. An identical nipple on the opposite side of the chamber provided a vent for gases/vapors. Entry of vapors through the side of the chamber rather than through the front of the chamber is considered a worst-case arrangement because the vapors would not impinge directly on the coupons.

3.1.2 Collection Chamber

The purpose of the collection chamber will be to provide a means to collect and sample gases and/or liquids which might pass through a permeable coupon (i.e., concrete*) during testing. This chamber was also constructed of stainless steel with a lid, sump, and gasket arrangement similar to the exposure chamber.

3.1.3 Coupon Holder

The coupon holder served to hold the coupons in such a manner as to subject one planar surface to the environment of the exposure chamber and the opposite planar surface to the collection chamber while providing a seal to the opening connecting the two chambers. This holder was fabricated to hold a variety of coupons ranging in thickness from a 14-gauge steel coupon to a concrete coupon as thick as one-half inch.

The coupon holder assembly shown in Figure 4, consisted of a front plate and a retainer. The front plate was a 1/4-inch thick, 7-inch square stainless steel plate with a 4-inch ID annular opening. Four 1/4 x 20 bolts were mounted around the back of the plate. The bolts served to hold a retaining plate in place and to provide the force necessary to compress an O-ring which created the seal between the exposure and the collection chambers.

* The collection chamber will be used in subsequent studies on the decontamination of concrete.

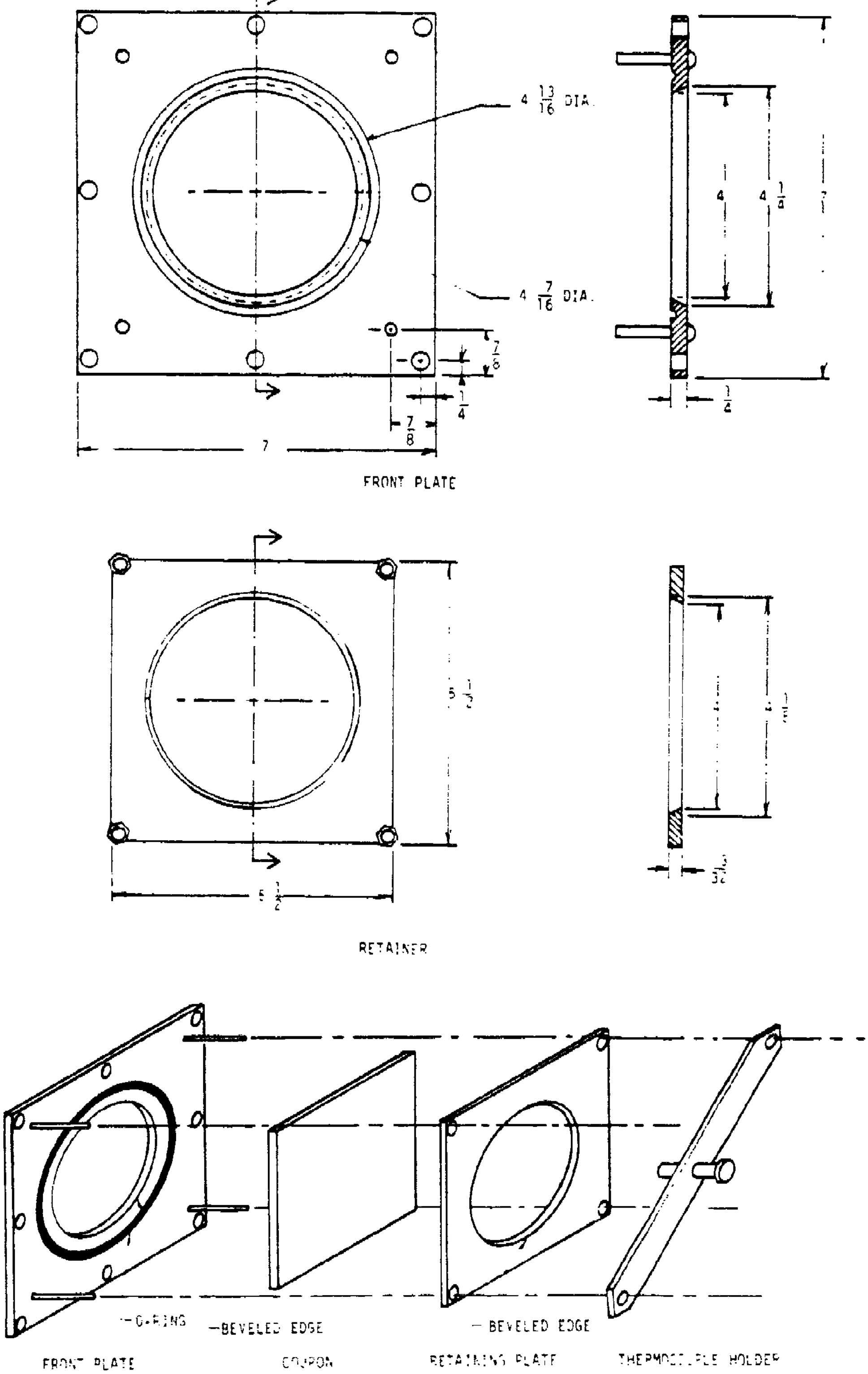

FIGURE 4. COUPON HOLDER ASSEMBLY

The O-ring was mounted in a groove milled into the wall of the front plate around the annular opening. Neoprene O-rings were used during the OPAB, Steam, Flashblast and Vapor Circulation experiments. A compressed asbestos gasket was used in place of the neoprene O-rings during the Hot Gases experiments.

3.2 Coupon Description

The coupons used in the Subtask 5 tests consisted of 14 gauge, 304 stainless steel. Each coupon measured 5 inches by 5 inches.

3.3 Coupon Spiking Method

Subtask 5 experiments were performed in Battelle's Toxic Substances Laboratory (TSL) rather than the Hazardous Materials Laboratory (HML). Performance of experiments in the TSL required the use of dilute solutions of agent at the following maximum surety concentrations:

VX = 1mg/ml
GB = 2mg/ml
HD = 10mg/ml

The dilute agent solution was applied to the coupon and the solvent (hexane or methylene chloride) was allowed to evaporate in order to have a contaminated surface representative of field conditions (i.e., solvent not present). Because agent may be volatilized along with the solvent during spiking, baseline experiments were performed to determine the amount of applied agent which can be recovered by extraction after the spiking sequence. It is important to note that previous work on recovery of agents from the coupons of interest was performed in the Hazardous Materials Laboratory (HML) because neat agent was used for spiking.(1)

The amount of solution required to spike the coupon was determined as follows. Assuming that the solvent used to extract the coupon following the decontamination treatment is concentrated to a volume of 5 ml, a total of 10 µg of agent is detectable by gas chromatography (GC)*. Therefore, for

* Lower detection limit of GC for all agents is about 2µg/ml.

determination of a destruction efficiency of about 99.9 percent, a total of 10 mg of agent must be initially applied to the coupon. A three order of magnitude difference between initial and anticipated final agent concentration is sufficient to allow determination of decontamination effectiveness. (Also, higher destruction efficiencies may be extrapolated, if desired, from the rate data obtained in the experiments.) Thus, in order to spike the coupon with 10 mg of agent, a total of 1 ml of dilute HD solution; 5 ml of dilute GB solution; or 10 ml of dilute VX solution must be applied to each coupon.

In the baseline experiments, stainless steel coupons were spiked with 10 mg of HD, GB or VX using dilute solutions of the respective agent. After the solvent had evaporated, the coupons were extracted with 50 ml of methylene chloride. The methylene chloride was concentrated to a volume of one ml and the concentrate was analyzed for agent. Results of the baseline experiments, shown in Table 1, are reported as recovery efficiencies. Recovery efficiency is the fraction of spiked agent recovered by extraction. The high recovery efficiencies shown in Table 1 demonstrate that spiking stainless steel coupons with dilute agent solutions was feasible. The average recovery efficiencies were used in subsequent analyses to calculate the decontamination efficiency as follows:

$$\text{Residual Agent on Decontaminated Coupon (mg)} = \frac{\text{Result of GC Analysis (mg)}}{\text{Recovery Efficiency}}$$

$$\text{Decontamination Efficiency (\%)} = \left(\frac{\text{10 mg - Residual Agent on Decontaminated Coupon}}{\text{10 mg}}\right) \times 100$$

3.4 Analytical Methodology

The samples generated from an experiment which were quantitatively analyzed for agent included 1) stainless steel coupons, 2) impinger solutions, 3) condensates and 4) chamber rinse solution. The following analytical procedures were used. Analytical procedures are detailed in Battelle Laboratory Record Book No. 39546.

TABLE 1. AGENT RECOVERY EFFICIENCIES BY EXTRACTION WHEN SPIKING STAINLESS STEEL COUPONS WITH DILUTE AGENT SOLUTIONS

Agent	Solution Spiked (ml)	Spiked Agent/ Coupon (mg)	Extracted Agent/ Coupon (mg)	Average Recovery Efficiency*
HD	1	10	10.4	0.85
			8.2	
			7.0	
GB	5	10	7.4	0.79
			8.8	
			7.5	
VX	10	10	5.4	0.58
			6.0	
			5.9	

$$* \text{ Average Recovery Efficiency} = \frac{\text{Average Agent recovered (mg)}}{\text{10 mg}}$$

3.4.1 Coupons

The stainless steel coupons were individually extracted by immersion in 50 mls methylene chloride. The coupons were allowed to soak for about 5 minutes. The methylene chloride was collected and then concentrated to one ml using a Kuderna-Danish evaporative concentrator prior to analysis.

The concentrate was analyzed by either a Carlo Erba Gas Chromatograph equipped with a Flame Ionization Detection (FID) system or a Hewlett Packard Gas Chromatograph equipped with a Flame Photometric Detection (FPD) system* and a Hewlett Packard Autosampler. Both chromotographs were equipped with a 30 meter glass capillary column coated with SE-52 phase. Data handling and storage was accomplished with a Hewlett Packard 1000 computer using CIS cals software.

Standard solutions containing known concentrations of agent (e.g., 10 ppm, 1 ppm, 0.1 ppm) were regularly used for preparation of calibration curves. The standards were analyzed at the same conditions as the samples.

3.4.2 Impingers

Impingers were used either to collect vaporized agent contained in the chamber exhaust stream (Hot Gas and Flashblast concepts) or to condense vapor exhausted from the chamber (Steam and Vapor Circulation concepts). For the Hot Gas and Flashblast Concepts, ethylene glycol diacetate (EGDA) solution was used in impingers for HD experiments while pH 3.7 distilled water was used in the GB and VX experiments.

Following an experiment, the solutions in the impingers were combined. The volume was recorded and the solution was then stored at -5 C until analysis could be completed.

The EGDA used for the collection of HD was analyzed for the presence of HD by Gas Chromatography/Hall detection. This procedure gave a detection limit of 0.2 μg/ml. The EGDA was analyzed without prior concentration.

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* Phosphorus mode for GB and VX.

The 3.7 pH water was analyzed directly for presence of VX and GB using a Technicon Autoanalyzer. The Technicon procedure for GB and VX gave a detection limit of at least 0.01 μg/ml. The 3.7 pH water was analyzed without concentration.

3.4.3 Condensate/Rinses

The condensate samples from the Steam tests and water samples collected from the Hot Gases tests were extracted in a two-liter separatory funnel. The condensate was loaded into the separatory funnel and washed with three separate 50 ml volumes of methylene chloride. The wash samples were combined and concentrated to one ml using the Kuderna-Danish appartus. The concentrate was then analyzed in the same method as the coupon extract.

The FREON 113 condensate samples were concentrated to approximately 5 mls using a rotary vacuum evaporator. The 5 ml aliquot was then transferred to the Kuderna-Danish concentrator for further concentration to 1 ml. The concentrate was then analyzed in the same method as the coupon extracts.

The chamber rinse samples (isopropyl alcohol and/or hexane) were collected and concentrated to one ml using the Kuderna-Danish concentrator. The concentrate was then analyzed in the same method as the coupon extracts.

3.5 Test Procedures

The approaches used to implement the five decontamination concepts were outlined in Test Plans. Test Plan Part A details the Hot Gases and the Vapor Circulation/RADKLEEN concepts, Test Plan Part B details the Steam, OPAB and Flashblast concepts.

4.0 HOT GASES DECONTAMINATION CONCEPT

The Hot Gases concept employs the use of heated gases such as burner exhaust gases to thermally decontaminate a building.[2] The circulation of inert hot gases in a building may allow the building to behave like an oven

such that the agent contaminant is exposed to elevated temperatures (100 to 300 C) for sufficient time to cause volatilization and/or thermal decomposition. The purpose of the experiments described below was to determine the decontamination effectiveness of the Hot Gases concept by subjecting stainless steel test coupons contaminated with agent to a hot-gas composition near that of a combustion exhaust gas.

4.1 Description of Hot Gases Experiments

4.1.1 Hot Gases Apparatus

The hot gas system is illustrated in Figures 5 and 6. In the process, a mixture of nitrogen, carbon dioxide, and water vapor were used as the hot gas source. This mixture was selected to represent the atmosphere produced when using stoichimetric combustion of natural gas to supply heat for field application. For stoichiometric combustion of natural gas in air, the molar fraction of products formed are 0.71 N_2:0.19 H_2O:0.10 CO_2. A gas mixture in this proportion was prepared by passing 1.7 nM^3/hr of N_2 and 0.24 nM^3/hr of CO_2 through a column of water heated at about 64 C. At this temperature, the vapor pressure of water (186 mm Hg) was such that the gas mixture exiting the water column had the desired molar proportion of gases. During the experiments the water column temperature was varied, depending on the outlet pressure of the water column (typically 207 mm Hg) and the flow rates of nitrogen and carbon dioxide (typically 2.0 nM^3/hr and 0.3 nM^3/hr, respectively) such that the desired molar ratio of gases was maintained.

Following the water column, the gas mixture was passed through a tubular furnace containing a pipe, packed with alumina pellets. The alumina pellets enhanced heat transfer from the furnace to the gas stream and served as a heat sink which increased the stability of the system with respect to temperature control. Following the tubular furnace, the hot gas stream was directed through a heated pipe and into the side of the insulated test chamber. In the chamber, heat was transferred from the gas stream to the test chamber and the stainless steel coupons. The gases were then exhausted from the chamber, through a water cooled heat exchanger and into a water trap. The water trap served to eliminate water condensate from the gas stream. The gas stream was then directed through two parallel impinger trains each comprised

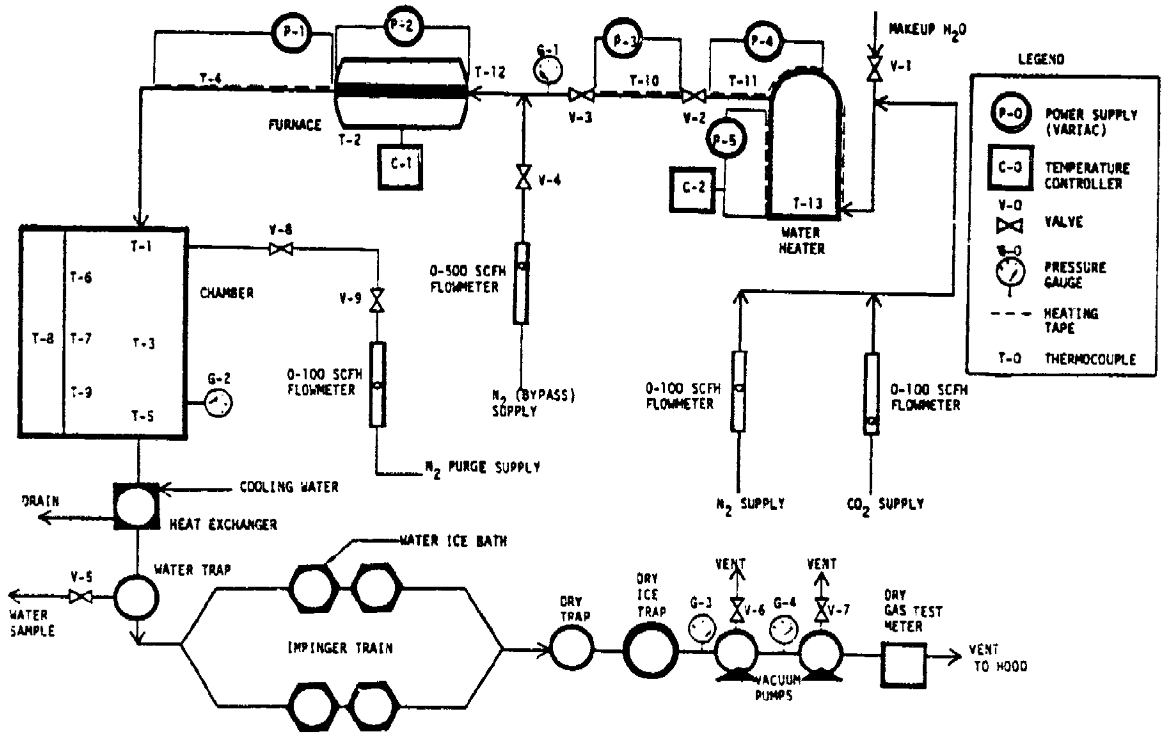

FIGURE 5. HOT GASES CONCEPT EQUIPMENT ARRANGEMENT

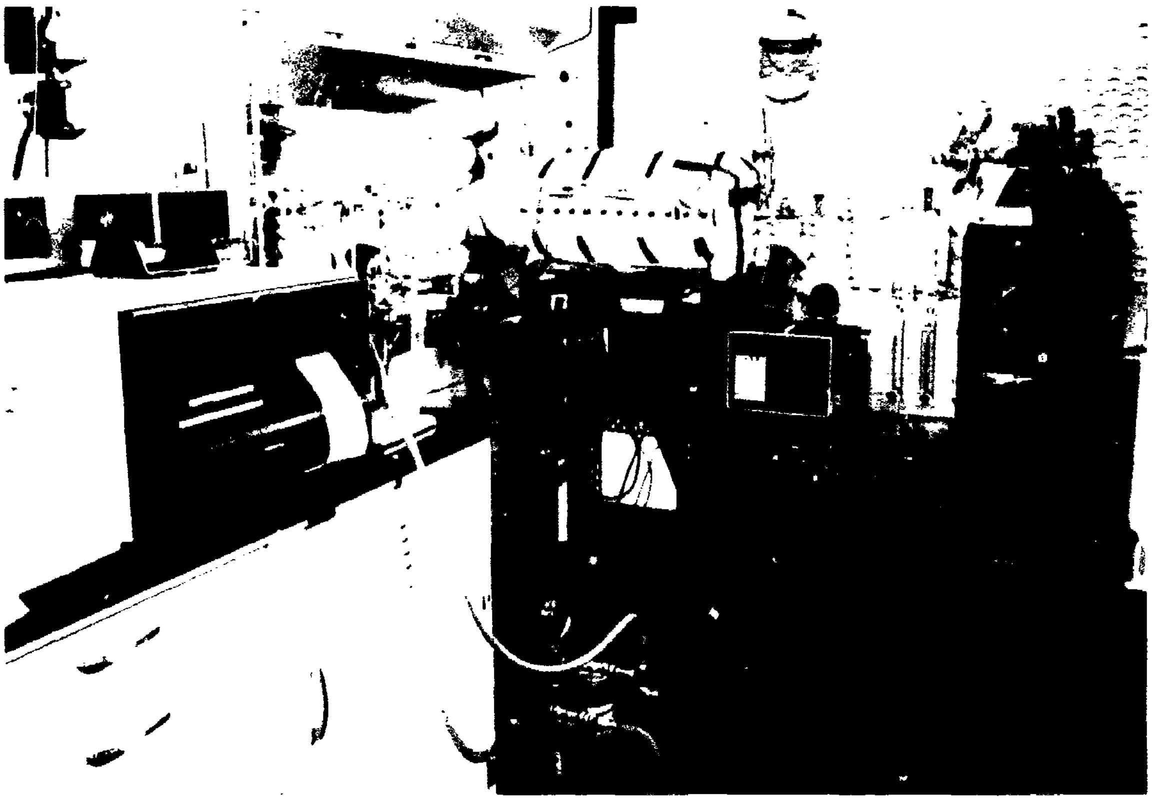

FIGURE 6. HOT GAS DECONTAMINATION EQUIPMENT CONFIGURATION

of two impingers in series. The impingers contained glass beads to aid dispersion of the gas and either pH 3.7 water for GB and VX or ethylene glycoldiacetate (EGDA) for HD to qualitatively trap agent that had volatilized from the coupons. The impinger trains were externally cooled with ice water during the experiment.

Residual water vapor was removed by passing the gas stream exiting the impingers through a trap cooled with solid carbon dioxide. The dryed gas was directed through two vacuum pumps in series, through a totalizing dry gas test meter, and finally to the hood. The vacuum pumps served to maintain the exposure chamber at a slightly negative pressure (about minus one inch of water column).

4.1.2 Test Variables

The primary test variables were the coupon temperature and time at temperature. Several methods of measuring the coupon temperatures were analyzed during the performance tests. The methods included having a metal-sheathed thermocouple probe touching the surface, attaching an unsheathed thermocouple to the surface with Sauereisen high temperature cement, etc. The preferred method involved the use of a bolt attached to a metal bar which, in turn, was attached to the back of the coupon holder as shown in Figure 4. The bolt supplied pressure to hold the thermocouple in place on the back of the coupon and to maintain the thermocouple in good contact with the coupon.

4.1.3 Test Procedure

Three stainless steel coupons were placed in coupon holders and then each coupon was spiked with 10 mg of agent using dilute agent solution. Three coupons were used to obtain triplicate determination of decontamination effectiveness in one experiment. The coupon holders were bolted into the chamber and the chamber lid was secured. The hot gas flow was started and regulated during the experiment such that the coupons were heated to the desired temperature. The initial set of experiments focused on heating the coupons to about 572 F (300 C). This required maintaining the gas temperature

inside the chamber at about 650 to 750 F (350 to 400 C). Once the coupons reached 300 C, the gas flow was regulated such that the coupons were maintained at about 300 C either for at least 30 seconds when HD was the contaminant; for at least 70 seconds when GB was the contaminant; or for at least 9.5 minutes when VX was the contaminant. These times were based on twice the time required to achieve 99.9 percent decomposition of the agent at 300 C.[2] After the required time at temperature was achieved, the hot gas flow was stopped and the chamber was allowed to cool overnight. The following day, the coupons and impingers were removed for analysis. The chamber was then rinsed with hexane which was also collected for analysis. It is important to note that because impermeable coupons (stainless steel) were used, the collection chamber was not monitored for agent during these tests.

4.1.4 Measurements

The following samples from each Hot Gas experiment were quantitatively analyzed for residual agent:

- Coupons (three separate analyses)
- Impingers (combined liquids from all four impingers)
- Water trap (combined water samples taken throughout the experiment)
- Chamber rinse.

Measurements made during the experiment included:

- CO_2 and N_2 flow rates
- Water column temperature
- Furnace inlet pressure
- Furnace inlet and exit temperature
- Chamber pressure
- Chamber inlet, internal and exit temperatures
- Time versus temperature profile for each coupon during heating and during cooldown
- Variac control settings
- Dry test meter reading
- Water trap sampling time and total amount of liquid collected

4.2. Discussion of Results from Hot Gas Decontamination Experiments

The results from the hot gas experiments are discussed in the following section. Actual data obtained from the experiments are recorded in Battelle Laboratory Record Book No. 39108.

Table 2 gives a summary of the operating conditions for the hot gas experiments.

A comparison of the total flow of gas into the system with the total flow of gas out of the system indicates that leakage of air into the system occurred during the experiments as planned. Leakage occurred primarily during the process of removal of condensed water from the cooled chamber exhaust stream. A small amount of leakage also occurred through the chamber lid gasket. (In field decontamination, it is important to note that because a building cannot be completely sealed, leakage will occur during implementation of the hot gas concept. As such, the building should be maintained at a slightly negative pressure because it is desirable to have air leakage into the building rather than leakage of gas potentially containing agent out of the building during operations.)

A summary of the coupon decontamination results from the six hot gas experiments is shown in Table 3. All coupons were decontaminated to below the detectable limit in each of the hot gas tests except the GB experiment conducted at 300 C. However, the subsequent GB experiment in which a lower operating temperature was employed (i.e., 150 C) resulted in decontamination to below the detectable limit. This suggests that GB detected in the 300 C experiment may not be GB but rather a thermal decomposition product which interferes with GB determination by GC analysis. The sample which showed "GB" was subjected to GC/MS analyses. Results of the GC/MS analyses, given in Table 4, substantiate the absence of GB but do not identify the analytical interference. Agent decomposition products were not detected in any of the coupon extracts subjected to GC/MS analysis. As such, if thermal decomposition occurs either the products volatilize from the surface or form a species which cannot be chromatogrammed. No obvious chars or other coatings on the

TABLE 2. SUMMARY OF OPERATING CONDITIONS FOR THE HOT GAS EXPERIMENTS

Hot Gas Experiment Number	Agent	Coupon Temperature Reached (C)	Time to Reach Temperature (min)	Time at Temperature (min)	Time to Cool Coupon to below 100F (min)	CO_2[a] Flow Rate (nM^3/hr)	N_2[a] Flow Rate (nM^3/hr)	H_2O[b] Flow Rate (nM^3/hr)	Total Flow into System (nM^3/hr)	Total Flow out of System[c] (nM^3/hr)	Chamber Pressure (mm Hg)
1	HD	300	382	7	600	0.23	1.73	0.45	2.41	2.32	+44.9
2	GB	300	270	5	540	0.25	1.98	0.54	2.78	4.19	-2.8
3	VX	300	255	15	660	0.25	2.01	0.51	2.78	3.60	-3.7
4	HD	150	165	60	390	0.28	2.01	0.48	2.78	3.34	-3.7
5	GB	150	120	60	390	0.28	2.04	0.45	2.78	3.54	-0.9
6	VX	150	100	60	420	0.25	2.01	0.54	2.80	3.60	-1.9

a) Corrected for inlet pressure (See G-1 on Figure 5)

b) Calculated from the vapor pressure of water at the water heater temperature, the furnace inlet pressure and the CO_2 and N_2 flow rates.

c) Total flow out of system = Dry Test Meter Flow Rate + Water Vapor Flow Rate

TABLE 3. COUPON DECONTAMINATION RESULTS FROM SIX HOT GAS EXPERIMENTS

Hot Gas Experiment Number	Agent	Coupon Temperature Reached (C)	Time At Temperature (min)	Average Residual Agent On Decontaminated Coupons[a] (mg)	Average Decontamination Efficiency[b] (%)	Calculated Destruction Efficiency[c]
1	HD	300	7	< 0.0012	> 99.98	> 99.99
2	GB	300	5	0.046[d]	99.5	> 99.99
3	VX	300	15	< 0.009	> 99.91	> 99.99
4	HD	150	60	< 0.001	> 99.98	80
5	GB	150	60	< 0.003	> 99.97	60
6	VX	150	60	< 0.009	> 99.91	2

(a) $\text{Average Residual Agent on Decontaminated Coupons (mg)} = \dfrac{\text{Average Result of GC Analysis (mg)}}{\text{Recovery Efficiency}}$

(b) The decontamination efficiency is the percent removal/destruction of agent from the coupon surface. Based on 10 mg of agent spiked on each of three coupons used in each test, the average decontamination efficiency is given by:

$$\text{Average Decontamination Efficiency (\%)} = \left(\frac{10\ \text{mg} - \begin{array}{c}\text{Average Residual Agent}\\ \text{on Decontaminated Coupons}\end{array}}{10\ \text{mg}} \right) \times 100$$

(c) Calculated destruction efficiency based on kinetic expressions given in Reference 2. Destruction efficiency calculation includes the heating period and time coupons held at temperature.

(d) Average of three coupons (0.019, 0.043, 0.077 mg). GC/MS analysis indicated the absence of GB.

TABLE 4. MASS SPECTRAL DATA OF COUPON EXTRACTS FROM SUBTASK 5 STUDIES ON HOT GAS DECONTAMINATION OF STAINLESS STEEL

Agent Decontaminated	Compound Identified	Comments on Source of Compound
HD	Tridecane	Solvent impurity
	1-Methylnitrobenzoic acid	Solvent impurity
	Phthalate	Plasticizers
GB	Phthalates	Plasticizers
VX	Phthalates	Plasticizers

stainless steel coupon surfaces were observed following hot gas decontamination.

Agent destruction efficiencies, shown in Table 3, were calculated from the kinetic thermal decomposition expressions given in Reference 2. A comparison of the calculated destruction efficiencies with the observed coupon decontamination efficiencies for the experiments operated at 150 C indicates that thermal destruction accounts for only a fraction of the coupon decontamination efficiency. The remaining decontamination was probably caused by volatilization of undecomposed agent from the coupons. The volatilized agent would mix with the hot gas stream in the chamber which subsequently is exhausted from the chamber. Although the mixing of the hot gas (typically at a temperature of about 230 to 340 C) with the volatilized agent can cause partial thermal decomposition of the agent, sufficient time may not have been available to cause complete decomposition. As such, undecomposed agent would be observed in the impinger and/or water trap. Results of the impinger and water trap analyses (See Table 5), confirm that the hot gas exhaust stream contained undecomposed agent. In the case of HD, a relatively large fraction of the HD spiked on the coupons was recovered in the impingers (5.8 mg of HD was recovered in Experiment 4 out of 30 mg spiked).

It is important to note that operation at higher temperatures may not completely eliminate volatilization because volatilization may occur primarily during the heatup stage. Also, operation at higher temperatures would require additional fuel requirements and increase the probability of damage to the building. Thus, a method must be developed to remove volatilized agent from the exhaust gas when decontaminating a building in the field using the hot gas concept. The method can be as simple as recycling all of the exhaust gas through the burner that supplies the hot gas. Following incineration to ensure complete agent destruction, part of the flue gas stream can then be vented to the atmosphere with the remainder directed into the building being decontaminated.

Because agent was volatilized during the hot gas experiments, the contamination of previously uncontaminated areas of the test chamber was possible especially at cold spots within the test chamber. However, analyses of the chamber rinses (See Table 5) demonstrated that initially uncontami-

TABLE 5. IMPINGER, WATER TRAP AND CHAMBER RINSE ANALYTICAL RESULTS FROM THE HOT GAS EXPERIMENTS

Hot Gas Experiment Number	Agent	Coupon Temperature Reached (C)	Agent Found In Impingers (mg)	Agent Found In Water Trap (mg)	Agent Found In Chamber Rinse (mg)	Total Agent Volatilized[a] (mg)
1	HD	300	2.0	< 0.001[b]	< 0.001[b]	2.0
2	GB	300	0.003	< 0.002	< 0.002	0.003
3	VX	300	0.005	< 0.005	< 0.005	0.005
4	HD	150	5.8	< 0.001	< 0.001	5.8
5	GB	150	0.005	0.006	< 0.002	0.011
6	VX	150	< 0.005	< 0.005	< 0.005	< 0.015

a) Total agent volatilized = Agent in impingers + Agent in water trap + Agent in chamber rinse.

b) Below detection limit

nated areas of the chamber did not become contaminated. Application of the hot gas concept to field structures must consider prevention of cold spots within the building by, for example, the use of baffles or other flow directional devices which would cause turbulent mixing of the hot gases throughout the structure.

4.3 Hot Gas Concept Conclusions/Recommendations

Tentative conclusions based on evaluation of the data from the hot gas experiments are as follows:

- Stainless steel contaminated with GB, HD, or VX can be decontaminated to below the detectable limit by maintaining the contaminated steel surface at a temperature of 150 C for one hour
- Undecomposed agent volatilizes from the stainless steel coupons thereby requiring a method to remove/decompose agent contained in hot gas exhausted from a building
- Volatilized agent did not contaminate previously uncontaminated areas of the test chamber.

Based on the experimental results, further evaluation of the hot gas concept in Subtask 6 of Task 3 is recommended. The suggested starting conditions for decontamination of painted mild steel, painted stainless steel, and unpainted mild steel coupons in Subtask 6 are 60 minutes at a coupon temperature of 150 C. It is anticipated that the effluent gas will be incinerated to destroy residual agent.

5.0 STEAM

The steam concept employs the use of ambient pressure steam to decontaminate a building by either chemical hydrolysis and/or physical removal (i.e., solubilization or evaporation) of agent contaminants.[2] Steam may be applied either manually or remotely (i.e., injecting steam into a

sealed building). The purpose of the experiments described below was to determine the decontamination effectiveness of steam by subjecting stainless steel test coupons contaminated with agent to steam.

5.1 Description of Steam Experiments

5.1.1 Steam Apparatus

The steam system is illustrated in Figure 7. Water was vaporized in pressure vessel at a rate of about 1.4 kg/hr. The steam at a pressure of about 50 to 200 mm Hg above atmospheric was directed through a heated pipe and into the side of the exposure chamber. The pipe was heated to prevent condensation of steam. In the exposure chamber, the steam condensed on the walls and the coupons. The condensate was directed from the sumps in the chamber to a collection flask. Uncondensed steam was vented from the chamber through impinger trains. The impinger trains, empty at the start of the experiment, were cooled in an ice bath such that the uncondensed steam exhausted from the chamber could be collected.

5.1.2 Test Variables

The primary test variable was the period of time that the stainless steel coupons were maintained at a temperature of about 100 C (212 F). Selection of the time at temperature allowed a comparison of the steam experiments to be made. The heat-up time (i.e., time required for the coupons to reach temperature) was not included because it varied in each experiment depending upon the steam flow rate.

The method used to measure coupon temperature is described in Section 4.1.2.

5.1.3 Test Procedure

Three stainless steel coupons were placed in coupon holders and then each coupon was spiked with 10 mg of agent using dilute agent solution.

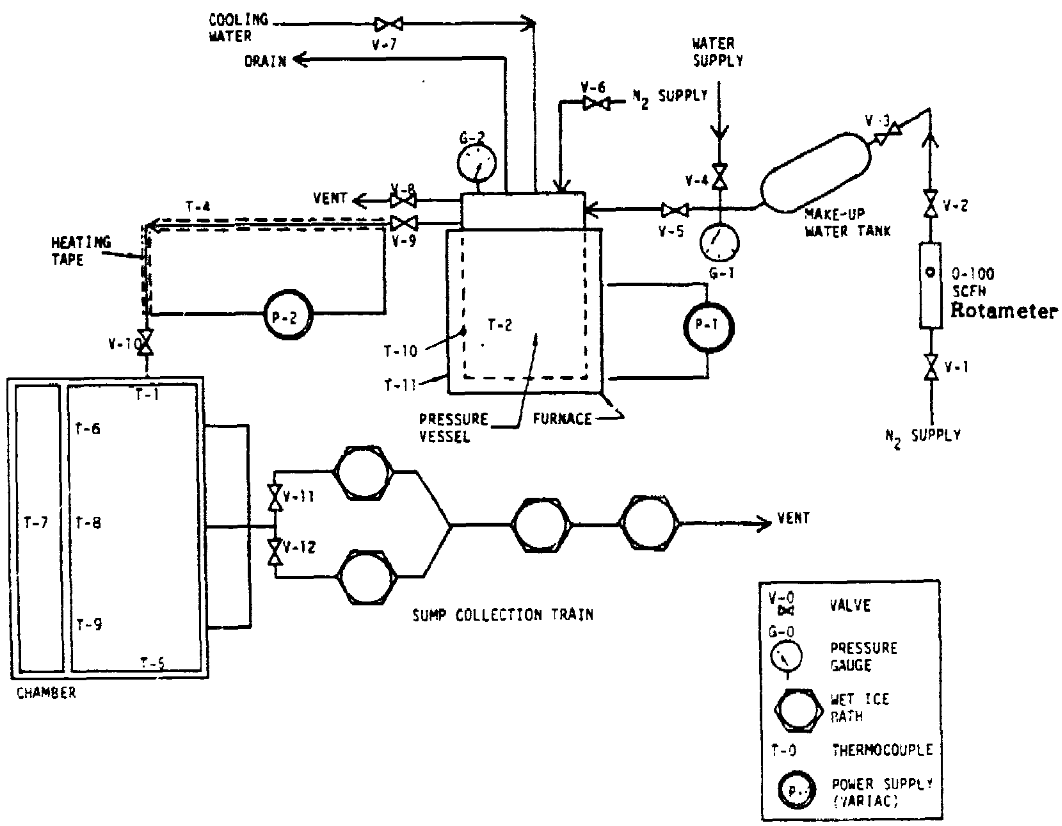

FIGURE 7. STEAM CONCEPT EQUIPMENT ARRANGEMENT

The coupon holders were bolted into the chamber and the chamber lid was secured. The steam flow was then started.

As steam condensed on the coupons, the coupons were heated from ambient temperature (about 20 C) to near the boiling point of water. In the initial set of experiments, steam flow was then maintained for an additional 20 minutes when HD was the contaminant; 60 minutes when GB was the contaminant; or 140 minutes when VX was the contaminant. These operation times were based on results from the Chemical Prescreening Studies[3] where decontamination with steam was evaluated in a closed system. Subsequent operation times were based on the results from the initial set of stainless steel decontamination experiments. After the required time at temperature was achieved, the steam flow was stopped and the chamber was allowed to cool overnight. The following day, the coupons and impingers were removed for analysis. The chamber was then rinsed with hexane which was also collected for analysis.

5.1.4 Measurements

The following samples from each steam experiment were quantitatively analyzed by GC for residual agent:

- Coupons (three separate analyses)
- Impingers (combination of liquid from both impingers)
- Condensate (combination of water samples taken throughout the experiment)*
- Chamber rinses (Isopropyl alcohol rinse followed by a hexane rinse).

Measurements made during the experiment included:

- Time versus temperature profile for each coupon during the experiment
- Inlet steam temperature

* In Experiments 4 and 6, two condensate samples were analyzed. One sample was condensate collected during the heat up period. The second sample was condensate collected between the time the coupons reached about 100 C and the end of the experiment.

- Pressure vessel temperature/pressure
- Variac control settings
- Condensate sampling time and amount collected
- Amount of liquid collected in the impingers.

5.2 Discussion of Results from the Steam Experiments

The results of the steam experiments are discussed in the following section. Actual data obtained from the experiments are given in Battelle Laboratory Record Book No. 39108.

Table 6 gives a summary of the operating conditions for the steam experiments. The average steam flow for the six steam experiments corresponds to a flow of about 20.8 kg of steam/m^3/hr for the 0.07 cubic meter chamber. Application of the steam concept to decontamination of field structures will require a lower steam flow rate per unit volume which, consequently, will require operation for a longer period than that shown in Table 6 because of longer heatup times. However, the time the stainless steel surfaces are maintained at about 100 C can correspond to the times shown in Table 6.

A summary of the coupon decontamination results from the six steam experiments are shown in Table 7. The results indicate that all coupons were decontaminated to below the detectable limit in each of the steam experiments. Decontamination of the coupons involved not only destruction of agent, but also physical removal of agent. In the steam experiments, agent can be physically removed from the coupons by either volatilization and/or washed off by steam condensation. Results from the analysis of the impinger samples shown in Table 8 indicate that undecomposed agent did volatilize from the coupons. The volatilized agent was exhausted from the chamber to the impingers along with uncondensed steam. It appears that insufficient contact time of the volatilized agent with the steam was available to cause complete agent destruction. As such, a method must be developed to remove volatilized agent from the exhausted steam when decontaminating a building using steam. The method can entail recycle of the exhausted steam to the steam generator.

TABLE 6. SUMMARY OF OPERATING CONDITIONS FOR THE STEAM EXPERIMENTS

Steam Experiment Number	Agent	Time to Reach Temp.[a] (min)	Time at Temp. (min)	Total Experiment Time (min)	Condensate Collected in Sump (ml)	Condensate Collected in Impingers (ml)	Total Condensate Collected (ml)	Steam Flow Rate kg/hr
1	HD	88	20	108	1446	380	1826	1.25
2	GB	30	60	90	1360	350	1710	1.14
3	VX	50	120	170	4050	650	4700	1.66
4	HD	65	40	105	2760	1050	4810	2.18
5	GB	50	60	110	2430	230	2660	1.45
6	VX	40	180	220	4565	470	5035	1.37

a) Time for coupons to reach about 100 C (boiling point of water)

TABLE 7. COUPON DECONTAMINATION RESULTS FROM SIX STEAM DECONTAMINATION EXPERIMENTS

Steam Experiment Number	Agent	Coupon Temperature Reached (°C)	Time At Temperature (min)	Average Residual Agent On Decontaminated Coupons[a] (mg)	Average Decontamination Efficiency[b] (%)
1	HD	100[c]	20	< 0.0012	> 99.98
2	GB[d]	100	60	< 0.006	> 99.94
3	VX	100	140	< 0.009	> 99.91
4	HD	100	40	< 0.0012	> 99.98
5	GB	100	60	< 0.006	> 99.94
6	VX	100	180	< 0.009	> 99.91

(a) $\text{Average Residual Agent on Decontaminated Coupons (mg)} = \dfrac{\text{Average Result of GC Analysis (mg)}}{\text{Recovery Efficiency}}$

(b) The decontamination efficiency is the percent removal/destruction of agent from the coupon surface. Based on 10 mg of agent spiked on each of three coupons used in each test, the decontamination efficiency is given by:

$$\text{Average Decontamination Efficiency (\%)} = \left(\frac{10\text{ mg} - \begin{array}{c}\text{Average Residual Agent}\\ \text{on Decontaminated Coupons}\end{array}}{10\text{ mg}}\right) \times 100$$

(c) Boiling point of water.

(d) Three mild steel coupons rather than three stainless steel were used.

TABLE 8. IMPINGER, SUMP CONDENSATE AND CHAMBER RINSE ANALYTICAL RESULTS FROM THE STEAM EXPERIMENTS

Steam Experiment Number	Agent	Time at Temperature (min)	Agent Found in Impingers (mg)	Agent Found in Sump Condensate (mg)	Agent Found in Chamber Rinses (mg)	Total Agent Physically Removed[a] (mg)
1	HD	20	0.030	0.030	0.003	0.063
2	GB	60	0.013	0.264	< 0.005	0.277
3	VX	140	0.224	0.038	0.10	0.362
4	HD	40	< 0.0012	< 0.0012[b] 5.2[c]	< 0.0012	5.2
5	GB	60	0.042	0.042	0.016	0.10
6	VX	180	< 0.009	0.170[b] 0.110[c]	0.015	0.295

(a) Total physical removal of agent (evaporation and/or washed off by condensing steam) = Agent in impingers + Agent in sump condensate + Agent in chamber rinses.

(b) Amount of agent in the condensate collected between the start of the experiment and the time the coupons reached about 100C.

(c) Amount of agent in the condensate collected between the time the coupons reached about 100C and the end of the experiment.

Repeated recycle should provide sufficient contact time of undecomposed agent with steam to ensure complete destruction (see Reference 3).

The second method by which undecomposed agent can be physically removed from the coupons is by washing off by the steam condensation. Results from the analysis of the sump condensate shown in Table 8 substantiate that agent wash-off does occur. In an effort to determine when agent wash-off occurs during the process, two condensate samples were taken in each of Experiments 4 and 6. The first sample consisted of liquid collected between the start of the experiment and the time the coupons reached about 100 C. The second sample consisted of liquid collected between the time the coupons reached about 100 C and the end of the experiment. The samples were analyzed separately. The results shown in Table 8 suggest that agent wash-off can occur throughout the steam decontamination process. Because the sump condensate contains undecomposed agent, the condensate would require a subsequent treatment. The treatment can be identical to that previously described for the steam exhaust. For example, the condensate can be collected in a sump, pumped from the building to temporary storage tanks, and recycled to the steam generator. The cycle could be repeated until no agent is detected in the condensate.

Minor amounts of agent were found in the chamber rinses in several of the experiments. The source of the agent is probably attributed to residual agent in the condensate collection system. Subsequent steam experiments in Subtask 6 will attempt to verify the source of the contamination by separately collecting rinses of the condensate collection system and the chamber.

5.3 Steam Concept Conclusions/Recommendations

Tentative conclusions based on evaluation of the data from the steam experiments are as follows:

- Stainless steel contaminated with HD, GB, or VX can be decontaminated to below the detectable limit by maintaining the steel surface at a temperature near the boiling point of water for 40, 60 or 180 minutes, respectively.

- Steam decontamination includes the physical removal of undecomposed agent from the coupon by volatilization and wash-off. Thus, a method to remove/decompose agent contained in exhausted steam and condensate from a building is required.
- Volatilized agent contaminated either the condensate collection system or previously uncontaminated areas of the chamber. Further efforts are required to determine the path of the contamination.

Based on the experimental results, further evaluation of the steam concept in Subtask 6 is recommended. The suggested starting conditions for decontamination of painted mild steel, painted stainless steel and unpainted mild steel are as follows:

GB - 60 minutes at a coupon temperature of 100 C
HD - 40 minutes at a coupon temperature of 100 C
VX - 180 minutes at a coupon temperature of 100 C.

In addition to the experiments above, experiments in which condensate containing undecomposed agents is reboiled are suggested. The reboiled water would be analyzed for agent to confirm that recycle of water to decompose residual agent is feasible.

6.0 VAPOR CIRCULATION/RADKLEEN®

The vapor circulation/RADKLEEN concept is a combination concept which employs the vapor circulation method as a means of application of FREON® 113 (Trichlorotrifluoroethane) - the solvent used in the RADKLEEN process[2]. In the Vapor Circulation/RADKLEEN process, FREON 113 is applied to a building in a vapor phase. The vapor would condense upon contacting the cool building surfaces. The condensate would then solubilize the agent contaminants and the solvent laden with agent would be collected from a sump for treatment. The purpose of the experiments described below was to determine the decontamination effectiveness of the process by subjecting test coupons contaminated with agent to FREON 113 vapor. It is important to note that agent was not decomposed by this process but rather physically removed by

solubilization. The solvent containing agent would require subsequent treatment to decompose the agent.

6.1 Description of Vapor Circulation Experiments

6.1.1 Vapor Circulation Apparatus

The Vapor Circulation/RADKLEEN® system is similar to the Steam system illustrated in Figure 7. FREON 113 was vaporized in a boiler (boiling point = 48 C or 117.6 F) at a rate of about 1 to 2 kg/hr. The FREON vapor was then directed through a heated pipe and into the exposure chamber. The pipe was heated to prevent condensation. In the exposure chamber, the FREON vapors condensed, solubilized the agent from the coupons, and drained into the sumps for collection. In several experiments, uncondensed vapors were directed through empty impinger trains cooled with water-ice mixture to condense and remove residual FREON vapor before venting. In Experiments 1, 5, and 6, all flow was directed through the sump collection system.

6.1.2 Test Variables

The primary test variable was the period of time that the coupons were maintained at a temperature of about 48 C. Coupon temperatures were measured in the method described in Section 4.1.2.

6.1.3 Test Procedure

Three stainless steel coupons were placed in coupon holders and then each coupon was spiked with 10 mg of agent using dilute agent solution. The coupon holders were bolted into the chamber and the chamber lid was secured. The FREON vapor flow was then started. As FREON began to condense on the coupons, the coupons were heated to near the boiling point of FREON 113. In the initial set of experiments (Experiments 1, 2 and 3), the FREON flow was stopped and the experiment was ended when the coupon temperature reached about 48 C. Subsequent operation times were based on the results

of these initial experiments. For example, if incomplete decontamination was observed in the initial experiments, then the subsequent experiment was operated at longer times rather than higher temperatures. The selected decontaminant temperature (boiling point) was considered optimum and limiting. A higher temperature would not lead to solubilization of the agent because the FREON would be in vapor form.

If complete decontamination was observed in the initial experiments, then the subsequent experiment was conducted at similar conditions (i.e., same time at temperature).

After the required time at temperature was achieved, the FREON flow was stopped and the chamber was allowed to cool. The coupons and impingers were then removed for analysis. The chamber was rinsed with hexane which was also collected for analysis.

6.1.4 Measurements

The following samples from each FREON experiment were quantitatively analyzed for residual agent:

- Coupons (three separate analyses)
- Impingers (combined liquid from both impingers)
- Condensate (combined FREON samples taken throughout the experiment)*
- Chamber hexane rinse.

Measurements made during the experiment included:

- Time versus temperature profile for each coupon during the experiment
- Inlet temperature
- Pressure vessel temperature/pressure
- Variac control settings
- Condensate sampling time and amount collected
- Amount of liquid collected in impingers.

* In Experiments 1, 2, and 6 multiple condensate samples were collected and separately analyzed for agent.

6.2 Discussion of Results from the Vapor Circulation Experiments

The results of the Vapor Circulation decontamination experiments are discussed in the following section. Actual data obtained from the experiments are given in Battelle Laboratory Record Book No. 39108.

Table 9 gives a summary of the operating conditions for the vapor circulation experiments. The average FREON flow rate for the six vapor circulation experiments corresponds to a flow rate of about 53 liters of FREON/m^3/hr for the 0.07-cubic meter chamber. Application of the FREON to a field structure at this flow rate per unit volume is probably not feasible. A lower flow rate can be employed but this will require operation for longer times than that shown in Table 9 because of longer heat-up times.

A summary of the coupon decontamination results from the six vapor circulation experiments is shown in Table 10. The data indicates that the coupons contaminated with either GB or HD were decontaminated to below the detectable limit. However, incomplete decontamination was observed when coupons were contaminated with VX. A longer time at temperature than two hours may be required to decontaminate stainless steel coupons contaminated with VX using the vapor circulation concept. Other options include repetition of the thermal cycles.

Analytical results from the impinger, sump condensate and chamber rinse samples taken during the vapor circulation experiments are given in Table 11. Agent was detected in two of the experiments in which impingers were used. This suggests that agent was volatilized from the coupons during the treatment and was entrained in the FREON vapor exhaust stream. (As such, the vapors emanating from a building must be collected and treated to remove/decompose agent during field decontamination when using the Vapor Circulation concept.)

Results of the sump condensate analyses shown in Table 11, indicate that for most experiments, a large amount of agent was present. This was anticipated because the coupon decontamination mechanism of the vapor circulation concept is by solubilization of undecomposed agent. However, in Experiments 4, 5, and 6 less than a milligram of agent was found in the

TABLE 9. SUMMARY OF OPERATING CONDITIONS FOR THE VAPOR CIRCULATION EXPERIMENTS

Vapor Circulation Experiment Number	Agent	Time to Reach Temperature[a] (min)	Time at Temperature (min)	Total Experiment Time (min)	FREON Collected in Sump (ml)	FREON Collected in Impingers (ml)	Total FREON Colected (ml)	FREON Flow Rate kg/hr
1	HD	60	0	60	2385	0[b]	2385	1.38
2	GB	35	0	35	2080	1	2081	2.04
3	VX	40	0	40	1598	12	1610	1.38
4	HD	55	0	55	2560	700	3260	2.04
5	GB	65	0	65	3845	0[b]	3545	1.90
6	VX	45	120	165	8480	0[b]	8480	1.76

(a) Time for coupons to reach about 48 C (boiling point of FREON 113)

(b) Impingers were not used (All liquid/vapor was directed through the sump collection system).

TABLE 10. COUPON DECONTAMINATION RESULTS FROM SIX VAPOR CIRCULATION EXPERIMENTS

Vapor Circulation Experiment Number	Agent	Coupon Temperature Reached (C)	Time At Temperature (min)	Average Residual Agent On Decontaminated Coupons[a] (mg)	Average Decontamination Efficiency[b] (%)
1	HD	48[c]	0[d]	< 0.0012	> 99.98
2	GB	48	0	< 0.006	> 99.94
3	VX	48	0	1.61	83.9
4	HD	48	0	< 0.0012	> 99.98
5	GB	48	0	< 0.005	> 99.94
6	VX	48	120	0.36	96.4

(a) $\text{Average Residual Agent on Decontaminated Coupons (mg)} = \dfrac{\text{Average Result of GC Analysis (mg)}}{\text{Recovery Efficiency}}$

(b) The decontamination efficiency is the percent removal/destruction of agent from the coupon surface. based on 10 mg of agent spiked on each of three coupons used in each test, the decontamination efficiency is given by:

$$\text{Average Decontamination Efficiency (\%)} = \left(\frac{10\text{ mg} - \begin{array}{c}\text{Average Residual Agent}\\ \text{on Decontaminated Coupons}\end{array}}{10\text{ mg}} \right) \times 100$$

(c) Boiling point of FREON 113.

(d) Experiment terminated after coupon temperatures neared the boiling point of FREON 113.

TABLE 11. IMPINGER, SUMP CONDENSATE AND CHAMBER RINSE ANALYTICAL RESULTS FROM THE VAPOR CIRCULATION EXPERIMENTS

Vapor Circulation Experiment Number	Agent	Time at Temperature (min)	Agent Found in Impingers (mg)	Agent Found in Condensate (mg)	Agent Found in Chamber Rinse (mg)	Total Agent Physically Removed[a] (mg)	Agent Recovery[b] (%)
1	HD	0	(c)	2.16 1.25 (d)	0.034	3.44	11
2	GB	0	0.065	3.6 0.036 (d)	0.005	3.70	12
3	VX	0	1.9	27.6	0.184	29.68	104
4	HD	0	< 0.001	< 0.012	< 0.001	< 0.012	< 1
5	GB	0	(c)	0.005	0.016	0.02	< 1
6	VX	120	(c)	0.144 0.041 (d) 0.026 0.026	0.02	0.24	2

(a) Total Agent Physically Removed = Agent in impingers + Agent in sump condensate + Agent in chamber rinse.

(b) Agent Recovery (%) = $100 \times \frac{\text{Agent Removed + Residual Agent on Coupon}}{\text{3 coupons x 10 mg agent spiked/coupon}}$

(c) Impingers not used(all FREON vapor/condensate was directed through the sump condensate collection system).

(d) Multiple sump condensate samples were taken during the experiment. Each sample was separately analyzed for agent.

condensate. Low agent recoveries in these experiments may be accounted for by the following: 1) Agent may have been decomposed during the experiment through interaction with either boiling FREON or a FREON contaminant such as water. The FREON may have picked up water vapor either from the air, from residual water in the chamber and condensate collection system, or from the pressure vessel used to supply FREON vapor. 2) Agent may have volatilized from the condensate collection system. Although quantitative capture of agent in the condensate collection system was not anticipated, it is unlikely that all agent volatilized and passed through the system. 3) FREON may form an azeotrope with GB. As such, GB would be co-distilled with FREON during the concentration step of the analysis. Further efforts would be required to determine the fate of agent in the vapor circulation experiments; however, additional experiments are not warranted unless further evaluation of the vapor circulation concept is required in Subtask 6.

6.3 Vapor Circulation Concept Conclusions/Recommendations

Tentative conclusions based on evaluation of the data from the vapor circulation experiments are as follows:

- Stainless steel coupons contaminated with HD, or GB can be decontaminated to below the detectable limit by maintaining contaminated coupons in contact with FREON 113 vapor until the coupons are heated to about 48 C (i.e., boiling point of FREON 113).
- Stainless steel contaminated with VX can be partially decontaminated by maintaining the steel in contact with FREON 113 vapor for two hours after the stainless steel reaches 48 C.
- Undecomposed agent volatilizes from the coupons thereby requireing a method to remove/decompose agent contained in FREON vapor exhausted from a building.

Decontamination of field structures will require large quantities of FREON 113 especially if the structure is contaminated with VX. Although recycle of the FREON is possible, sizable evaporation losses are expected. Observations made during the vapor circulation experiments indicate that

FREON 113 readily evaporates at room temperature. Also, FREON 113 is relatively expensive.* As such, further evaluation of the vapor circulation concept at this time is not recommended. However, the vapor circulation concept should be retained in the event that a replacement concept is required for decontamination of GB or HD in Subtask 6.

7.0 FLASHBLAST DECONTAMINATION CONCEPT

The Flashblast Concept employs the use of high intensity light to decontaminate building surfaces.(2) The light, supplied from a high intensity xenon-quartz strobe light, generates sufficient heat on material surfaces to remove paint and rust and to thermally decompose surface contaminants. The purpose of the experiments described below was to determine the decontamination effectiveness of Flashblasting by subjecting stainless steel test coupons contaminated with agent to high intensity light pulses.

7.1 Description of Flashblast Experiments

7.1.1 Flashblast Aparatus

The Flashblast system is illustrated in Figure 8. A xenon micropulser was employed to supply pulses of energy to the quartz flash tube. The micropulser was capable of supplying up to a 100 joule pulse lasting about 1 to 10 microseconds at a rate of about 3 pulses per second. The pulses caused the quartz flash tube to emit light over a broad spectrum but primarily in the 2000 to 3000 Å regime (ultraviolet). The light was directed to a single stainless coupon located in the center of the chamber. A hemispherical flash tube assembly lined with COILZAK®** was used to hold the flash tube and direct the light to the coupon (see Figure 9). The flash tube assembly maintained

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* FREON 113 bulk quantity = $0.89/lb (Chemical Marketing Reporter, January 30, 1984).

** COILZAK is an aluminized flexible material with a reflectivity of 80 to 83 percent.

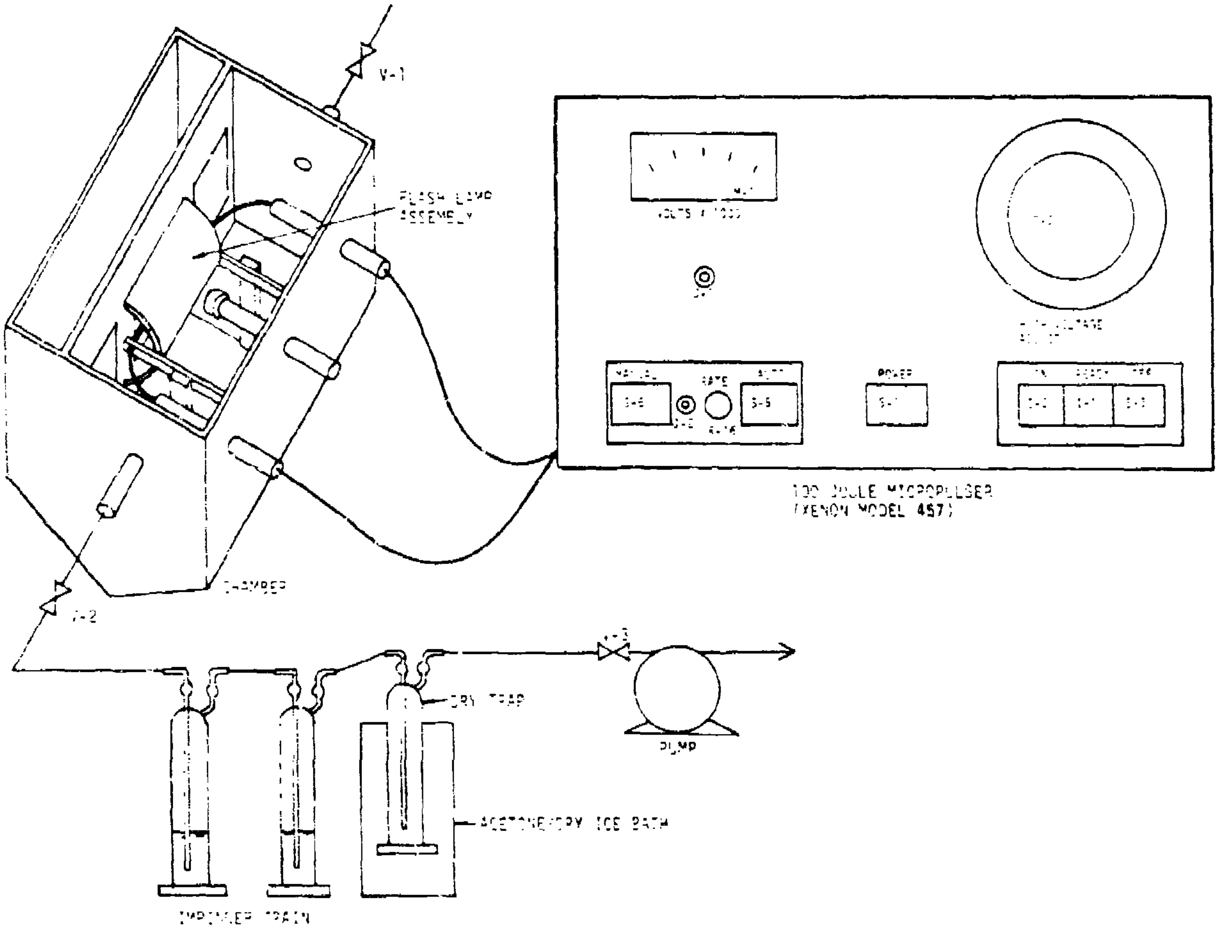


FIGURE 8. FLASHBLAST CONCEPT EQUIPMENT ARRANGEMENT

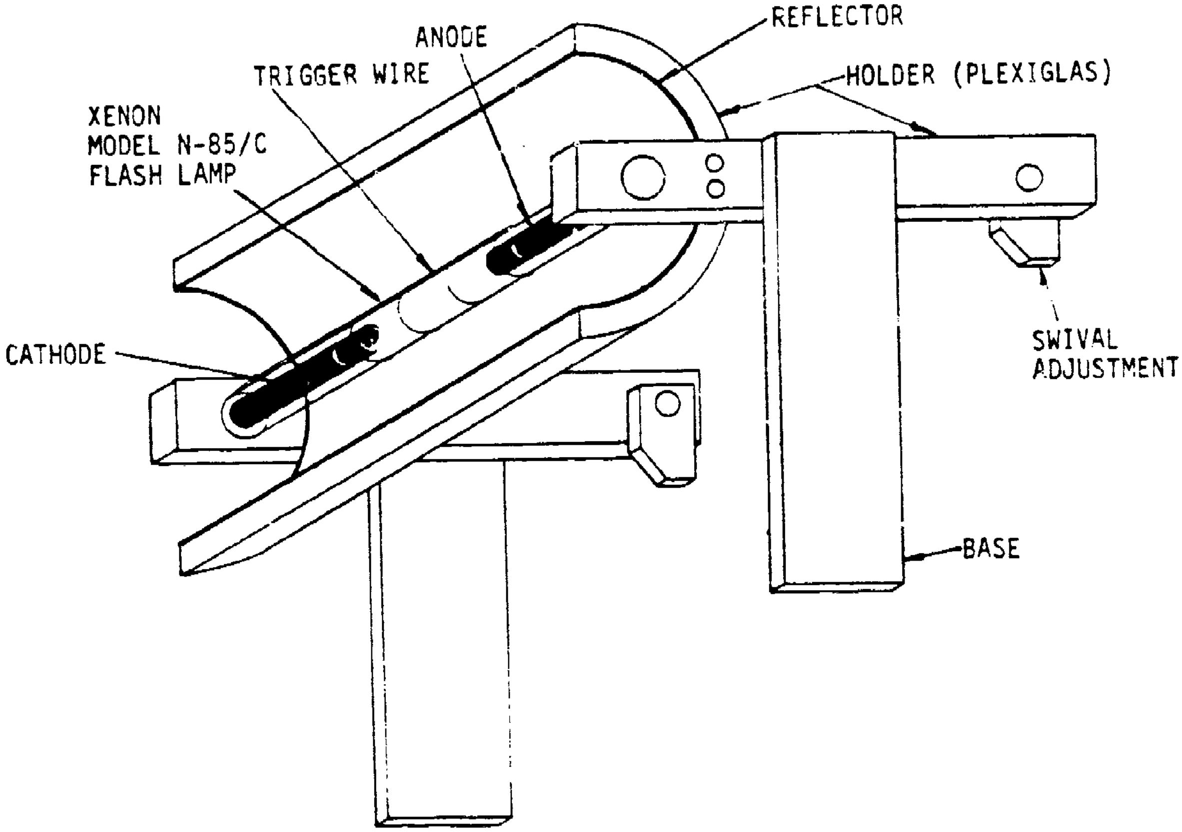


FIGURE 9. FLASHTUBE ASSEMBLY

the flash tube at a distance of 2.54 cm from the coupon. Only one coupon was decontaminated in each experiment because of constraints imposed by the size of the xenon-quartz flash tube.

The test chamber was exhausted during each experiment using a vacuum pump. It was necessary to exhaust the chamber because of unsealed openings into the chamber required for passage of the electrical leads. Ventilation was accomplished by withdrawing air from the test chamber using a vacuum pump. Impingers were used to trap volatilized agent from the air stream pulled through the chamber. The impinger trains contained either pH 3.7 water for GB and VX, or EGDA for HD.

7.1.2 Test Variables

The pr ary test variable was the total amount of energy supplied to the test coupon in the form of light. The supplied energy per pulse and the pulse rate were maintained approximately constant for all experiments. In order to vary the amount of power applied, the duration of the flashblasting was increased from 5 minutes for the initial series of experiments to 10 minutes for the final series. It is important to note that light intensity measurements were not performed during the experiments because of the undesirable configuration of the flash tube assembly and the test chamber. The amount of energy supplied to the coupon was calculated from the voltage and the capacitance of the micropulser assuming no loss by reflectance. However, energy losses occurred by 1) conversion of electricity to light (about 40 percent conversion); 2) absorbance by the reflector and test chamber; and 3) reflection from the surface of the stainless steel coupon.

7.1.3 Test Procedure

One stainless steel coupon was placed in a coupon holder. The coupon was then spiked with 10 mg of agent using dilute agent solution. The coupon holder was bolted into the center position of the chamber and the chamber lid was sealed. It is important to note that blank coupons attached to coupon holders were placed in the left and right positions of the chamber

during flashblasting. This prevented volatilized agent from contaminating the rear collection chamber (see Section 3.1.2).

After the chamber lid was secured, ventilation of the chamber was initiated. After about 5 minutes of ventilation, flashblasting was started and continued for either 5 minutes (first six experiments) or 10 minutes (last three experiments). Ventilation, which was maintained during flashblasting, was continued for about 10 minutes following the termination of flashblasting in order to purge the chamber of residual agent. The coupon was then removed for analysis. After a set of experiments on a particular agent was complete, the impingers were removed and the chamber was rinsed with hexane. The chamber rinse and impinger were then analyzed for agent.

7.1.4 Measurements

The following samples from each Flashblast experiment were quantitatively analyzed for residual agent:

- Coupon
- Impingers (combined liquids from both impingers)
- Chamber rinse

Measurements made during the experiments included:

- Pulse rate setting
- Voltage setting
- Ventilation/Flashblast times
- Coupon temperature.

7.2 Discussion of Flashblast Experimental Results

The results of the Flashblast experiments are discussed in the following section. Actual data obtained from the experiments are given in Battelle Laboratory Record Book No. 39108.

Table 12 gives a summary of the operating conditions for the Flashblast experiments. As shown in Table 12, the applied power was calculated to be about a total of 26 kw for each of the initial series of experiments. The total applied power was increased to about 49 kw for the final series of experiments in an effort to increase decontamination effectiveness.

TABLE 12. SUMMARY OF OPERATING CONDITIONS FOR THE FLASHBLAST EXPERIMENTS

Agent	Pulse Rate (Pulses/sec)	Operating Voltage (Volts)	Energy/Pulse (Joules)[a]	Number of Pulses	Total Power (kw)[b]	Total Experiment Time (min)[c]	Coupon Temperature Increase from (Degrees C)[d]
HD (1)	1	9400[e]	88	300	26	15	13
HD (2)	1	9200	85	300	26	20	12
GB (1)	1	9200[e]	85	300	26	20	22
GB (2)	1	9200	85	300	26	15	17
VX (1)	1	9200	85	300	26	20	20
VX (2)	1	9200	85	300	26	20	15
HD (3)	1	9000[e]	81	600	49	29	-
GB (3)	1	9000	81	600	49	25	16
VX (3)	1	9000[e]	81	600	49	25	-

(a) Energy/Pulse = $\frac{1}{2} CV^2$ where C = capacitance = 2×10^{-6} Farad, V = Volts

(b) Total Power (kw) = Energy/Pulse x Pulse Rate x Number of Pulses/1000

(c) Includes about 10 to 15 minutes of purge time.

(d) Temperature rise of coupon above initial 20 C caused by flashblasting.

(e) Arcing between the chamber and the flashblast lamp occurred on several of the pulses.

Flashblasting caused heating of the stainless steel coupons due to absorption of energy from the UV light pulses. The coupon temperature was raised by as much as 22 C during the second experiment with GB. In two experiments, temperature readings could not be obtained because of arcing which occurred on several of the pulses. Arcing resulted in a discharge of electricity from the flash tube to the test chamber producing faulty readings in the thermocouple touching the back surface of the stainless steel coupon. Arcing was probably caused by positioning the flash tube assembly too close to the coupon holder bolts in the test chamber.

A summary of the coupon decontamination results from the nine Flashblast experiments is given in Table 13. The results indicate that the decontamination efficiency was above 99 percent in each of the experiments. In two of the Experiments GB (2) and HD (3), the coupons were decontaminated to below the detectable limit.

It was anticipated that the method of decontamination of the coupons would involve destruction of the agent by the high intensity light. However, analysis of the impinger samples and chamber rinse samples from the experiments indicates that decontamination included volatilization of undecomposed agent from the coupons. The results of the impinger and chamber rinse analyses, given in Table 14, show that in Experiment GB (3), essentially no agent destruction occurred because 100 percent of the amount of GB spiked was recovered in the chamber rinse. It is unlikely that flashblasting alone was responsible for this degree of volatilization. Ventilation of the test chamber may have accounted for part of the volatilization. Further experiments are required to determine the affect of ventilation on the volatilization of agent from coupons installed in the test chamber.

7.3 Flashblast Concept Conclusions/Recommendations

Tentative conclusions based on evaluation of the data from the Flashblast experiments are as follows:

- Although the coupon decontamination efficiency was above 99 percent in all flashblast experiments, decontamination to below the detectable limit was observed in only two of the nine tests

TABLE 13. COUPON DECONTAMINATION RESULTS FROM NINE FLASHBLAST EXPERIMENTS

Agent	Total Power Supplied (kw)	Residual Agent on Decontaminated Coupons[a] (mg)	Decontamination Efficiency[b] (%)
HD(1)	26	0.004	99.96
HD(2)	26	0.002	99.98
GB(1)	26	0.026	99.7
GB(2)	26	< 0.005	> 99.95
VX(1)	26	0.066	99.3
VX(2)	26	0.041	99.6
HD(3)	49	< 0.0012	> 99.98
GB(3)	49	0.04	99.6
VX(3)	49	0.05	99.5

(a) Residual Agent on Decontaminated Coupons (mg) = $\frac{\text{Average Result of GC Analysis (mg)}}{\text{Recovery Efficiency}}$

(b) The decontamination efficiency is the percent removal/destruction of agent from the coupon surface. Based on 10 mg of agent spiked on one coupon used in each test, the decontamination efficiency is given by:

$$\text{Decontamination Efficiency (\%)} = \left(\frac{10\text{ mg} - \begin{array}{c}\text{Average Residual Agent}\\ \text{on Decontaminated Coupons}\end{array}}{10\text{ mg}} \right) \times 100$$

TABLE 14. IMPINGER AND CHAMBER RINSE ANALYTICAL RESULTS FROM THE FLASHBLAST EXPERIMENTS

Agent	Agent Found in Impinger (mg)	Agent Found in Chamber Rinse (mg)	Total Agent Volatilized (mg)
HD #1,2	0.540	0.002	0.542
GB #1,2	0.002	< 0.005	0.002
VX #1,2	0.0002	0.129	0.129
HD #3	0.160	0.003	0.163
GB #3	0.022	10.0	10.022
VX #3	0.0002	< 0.0001	0.0002

- Decontamination includes volatilization of undecomposed agent
- The coupon temperature increased during the experiments as a result of flashblasting.

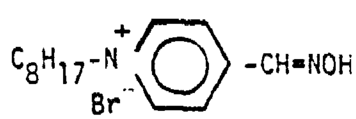
Based on the results of the flashblast experiments, further evaluation of the flashblast concept is not suggested because:

- A supplementary process which destroys volatilized agent is required for flashblasting
- High voltage (9,000+ volts) operation requires high power requirements when decontaminating large areas and special safety requirements for operating personnel (UV light and high voltage)
- Decontamination of complex building configurations is impractical because of the configuration of the flashblast lamp
- Because the flashblast lamp emits light in the UV range, the penetration of light into concrete and painted surfaces is expected to be minimal.

However, experiments involving ventilation of the test chamber containing spiked coupons are suggested. The experiments will serve as part of the baseline data.

8.0 OPAB DECONTAMINATION CONCEPT

The OPAB concept involves decontamination by spray application of an aqueous solution of 1-octyl-pyridinium 4-aldoxime bromide (OPAB), OPAB has the following chemical structure:



The specifications of the decontamination solution are as follows:

- 5 percent OPAB*
- 1 percent foam stabilizers
- 5 percent anti-freezing agent (poly-ethylene glycol)
- 89 percent water.

The selection of OPAB for experimental evaluation was based on studies performed at Battelle-Frankfurt (sponsored by the German Defense Ministry) which indicated OPAB to be highly effective in decontaminating VX. Beaker tests performed during the Chemical Prescreening Studies[(3)] demonstrated the effectiveness of OPAB in decontaminating GB and HD. The purpose of the experiments described below was to determine the decontamination effectiveness of OPAB on stainless steel coupons when applied in the form of a spray.

8.1 Description of OPAB Experiments

8.1.1 OPAB Application Apparatus

The OPAB application apparatus is illustrated in Figure 10. A 5 percent solution of OPAB was placed in a pressure vessel and the vessel was pressurized to 6.8 atm.** The OPAB solution was then directed through three identical spray nozzles.** The spray nozzles were oriented in the test chamber such that the spray from each nozzle completely covered one of the three test coupons (10.16 cm circle). Each nozzle provided a spray of coarse water particles (150 to 750 microns in diameter) at a flow rate of about 0.76 liter/min.**. This flow rate was maintained for a period of from one to two seconds for each spray application thereby providing a coverage** of about 1.5 to 3.0 liter/m^2 of coupon area/spray. Runoff liquid from spraying was drained into the sumps of the test chamber and then into collection vessels as illustrated in Figure 10.

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* A concentrated OPAB solution was obtained from Battelle-Frankfurt. The 5 percent solution was prepared from the concentrate by dilution of 1 part concentrate to 3 parts water.

** The supply pressure, nozzle type, flow rate and coverage were based on results from the Diffusion Studies[(4)].

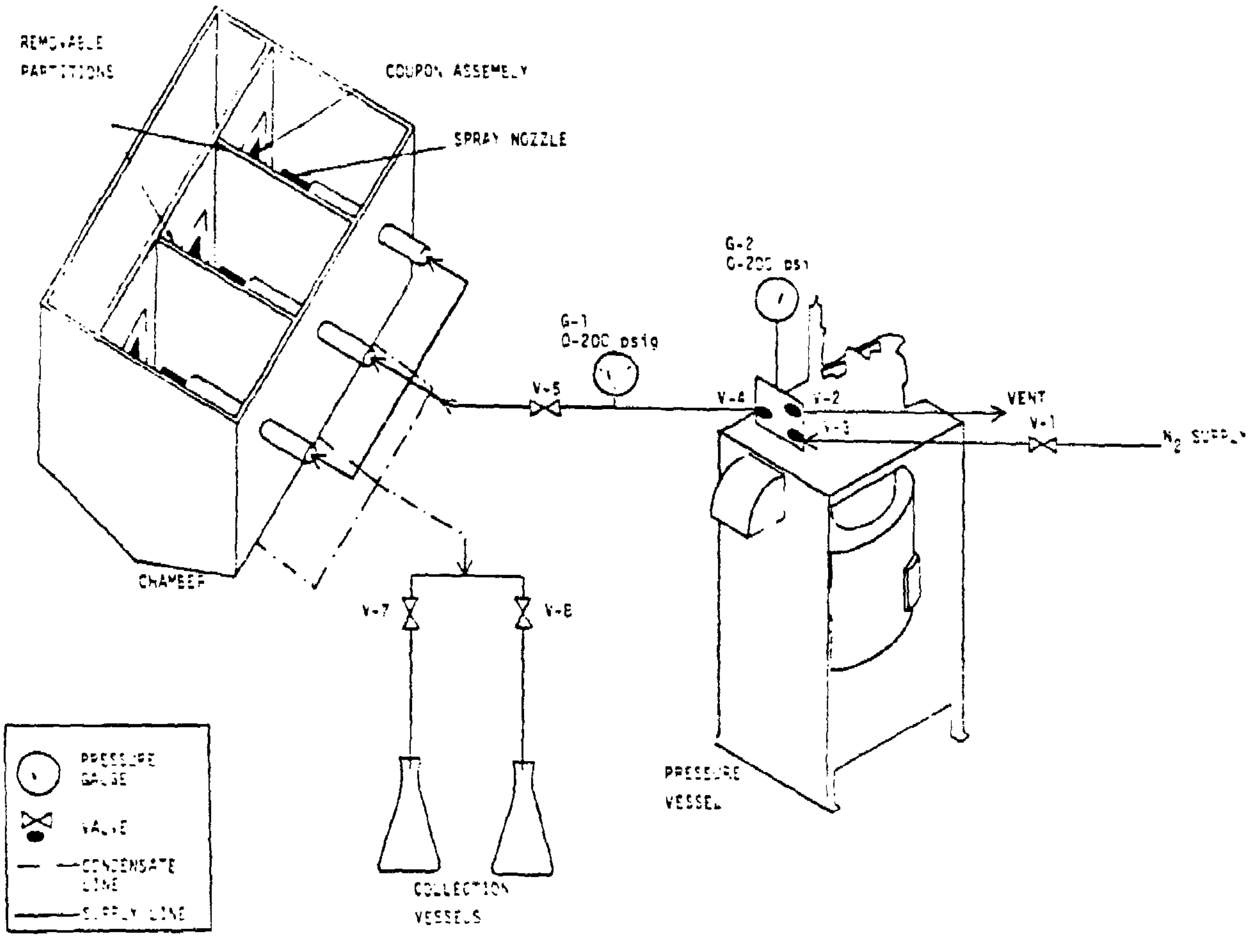

FIGURE 10. OPAB APPLICATION EQUIPMENT ARRANGEMENT

8.1.2 Test Variables

The nozzle type, supply pressure, flow rate and coverage were maintained approximately constant for all of the OPAB experiments. The primary test variables were then 1) the total number of sprays and 2) the time interval between sprayings. In the initial set of experiments, the spray application was repeated 10 times at 5-minute intervals. In the final set of experiments, the spray application was repeated 10 times at intervals suggested from results of the Chemical Prescreening Studies(3).

8.1.3 Test Procedure

Three stainless steel coupons were placed in coupon holders and then each coupon was spiked with 10 mg of agent using dilute agent solution. The coupon holders were bolted into the chamber and the chamber lid was secured. The spray application was then initiated and repeated ten times at the desired time interval.

Following completion of the sprayings, the coupons were removed from the chamber and the chamber was rinsed with isopropyl alcohol followed by hexane. Liquid collected in the sump of the test chamber was not analyzed directly but, rather, was stored for a sufficient period (i.e., overnight) to allow decontamination of undecomposed agent which may have been physically removed from the coupons by the action of the spray.

8.1.4 Measurements

The following samples from each OPAB experiment were collected for quantitative analysis of residual agent:

- Coupon (three separate analyses)
- Sump liquid (combined liquids collected throughout the experiment)
- Chamber rinse.

Measurements made during the experiment included:

- Supply pressure

- Amount of liquid collected in the sump collection system versus time
- Number of sprays
- Time interval for spraying.

8.2 Discussion of OPAB Experimental Results

The results of the OPAB experiments are discussed in the following section. Actual data obtained from the experiments are recorded in Battelle Laboratory Record Book No. 39108.

A summary of the operating conditions for the OPAB experiments is given in Table 15. As shown in Table 15, the desired coverage of 1.5 to 3.0 liter/m^2/spray was obtained for all experiments. It is important to note that blockage of the test chamber drain lines occurred during the second VX experiment. The blockage was caused by the formation of a precipitate in the spent OPAB solution. It is not known whether the precipitate had formed in the OPAB solution stored in the pressure vessel or as the OPAB was being sprayed.

A summary of the coupon decontamination results from the six OPAB experiments is given in Table 16. The results indicate that OPAB is highly effective in decontaminating GB contaminated stainless steel. High decontamination efficiencies were also observed for HD and VX. In the first series of experiments, a time interval of 5 minutes was selected based on results from the Diffusion Studies. Because incomplete decontamination was observed for VX and HD, the time interval was increased to allow more time for the OPAB to react with the agent on the coupon. Results from the Chemical Prescreening Studies(3) indicate that about 180 and 240 minutes are required to decontaminate VX and HD, respectively. As such, 10 sprays at a time interval of 18 minutes were selected as the conditions for the second VX experiment. Ten sprays at a time interval of 24 minutes were selected as the conditions for the second HD experiment. The results of the HD experiments indicate that increasing the time interval to 24 minutes resulted in an increase in the decontamination efficiency by an order of magnitude over the 5 minute time interval experiment. The data suggests that a further increase in the time

TABLE 15. SUMMARY OF OPERATING CONDITIONS FOR THE OPAB EXPERIMENTS

Agent	Total OPAB Sprayed (ml)	Spray Interval (min)	Number of Sprays	Calculated Coverage[a] liter/m^2/spray)	Experiment Time[b](min)
HD	563	5	10	2.3	50
GB	628	5	10	2.6	50
VX	517	5	10	2.1	50
HD	450	24	10	1.9	240
GB	392	5	10	1.6	50
VX	495[c]	18	10	2.0	180

(a) Calculated coverage = Total OPAB sprayed (ml) x 0.001 liter/ml/$\left[(0.1016)^2 \pi/4\right]$/ 10 sprays/3 coupons.
(b) Experiment time = Spray interval x number of sprays.
(c) Does not include about 50 to 100 ml of OPAB solution remaining in the test chamber following the experiment. A precipitate had formed in the OPAB solution which caused blockage of the test chamber drain lines.

TABLE 16. COUPON DECONTAMINATION RESULTS FROM SIX OPAB EXPERIMENTS

Agent	Time Interval Between Sprays (min)	Average Residual Agent (mg)	Average Decontamination Efficiency[b] (%)
HD	5	0.028	99.7
GB	5	< 0.0001[c]	> 99.999
VX	5	0.038	99.6
HD	24	0.003	99.97
GB	5	< 0.006	> 99.94
VX	18	0.126[d]	98.7[d]

(a) $\text{Average Residual Agent on Decontaminated Coupons (mg)} = \dfrac{\text{Average Result of GC Analysis (mg)}}{\text{Recovery Efficiency}}$

(b) The decontamination efficiency is the percent removal/destruction of agent from the coupon surface. Based on 10 mg of agent spiked on each of three coupons used in each test, the decontamination efficiency is given by:

$$\text{Average Decontamination Efficiency (\%)} = \left(\frac{10 \text{ mg} - \begin{array}{c}\text{Average Residual Agent}\\ \text{on Decontaminated Coupons}\end{array}}{10 \text{ mg}} \right) \times 100$$

(c) Interferences with GB analysis occurred when a conventional packed column GC-FID was used. The use of a capillary column GC-FPD eliminated the interference.

(d) OPAB solution may have degraded during spraying.

interval to 30-40 minutes should result in decontamination to below the detectable limit.

The results of the VX experiments indicate that the decontamination efficiency did not increase when the time interval was increased to 18 minutes. This can be explained as follows. In the second VX experiment, precipitate was formed in the OPAB solution which caused blockage of the chamber drain lines. The precipitate indicates that the OPAB solution may have partially degraded while in the supply vessel.* Although the OPAB may have degraded a high decontamination efficiency was observed. Further experiments using freshly prepared OPAB are required to substantiate the decontamination efficiency of OPAB for VX contaminated stainless steel.

Difficulties were encountered in the extraction/concentration of the sump samples from the OPAB experiments in preparation for analyses. Attempts to extract the aqueous sump samples with hexane were unsuccessful because OPAB (or its decomposition products) was extracted into the hexane phase. Subsequent attempts to concentrate the hexane by evaporation resulted in formation of a viscous liquid which could not be analyzed by GC. Concentration of the sump liquid without extraction was not possible because GB will boil over with the water which, in the form of steam, will destroy any residual GB.

The difficulties in extraction may be caused by either the degradation of OPAB solution or by the degree of concentration required in order to analyze the extracts. Previous studies involving relatively fresh OPAB[(3)] showed that extraction of OPAB solution with organic solvents were successful in that most of the OPAB remained in the aqueous phase. These studies involved extraction of 10 ml of OPAB solution with 10 ml of methylene chloride. The methylene chloride was then concentrated by solvent evaporation to about 1 ml.** In the stainless steel tests, however, much larger quantities of older OPAB solution (about 500 ml) required extraction with

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* It is important to note that the OPAB used in the tests was obtained from Battelle-Frankfurt (received October 1983) as a concentrate dissolved in water. OPAB may have a finite shelf-life in this form. The solid material should be stable.

** The concentrated extract was slightly colored indicating the presence of OPAB.

50 ml of solvent. Although even if fresh OPAB may be only slightly soluble in the organic solvent, the concentration of 50 ml of solvent to one ml could result in a concentrated solution of OPAB. OPAB, which is relatively non-volatile, would not be evaporated with the solvent during concentration.

Because of the concentration difficulties, no analyses of the sump liquid from the OPAB stainless steel experiments were performed. However, based on the Chemical Prescreening Studies,[(3)] it is unlikely that undecomposed agent would be found in the solutions. In field decontamination, the sump liquid could be allowed to stand for several days prior to reuse/disposal to ensure complete decomposition of residual agent.

8.3 OPAB Concept Conclusions/Recommendations

Tentative conclusions based on evaluation of the data from the OPAB experiments are as follows:

- Stainless steel contaminated with GB can be decontaminated to below the detectable limit by spraying with OPAB solution every 5 minutes
- Results suggest stainless steel contaminated with HD or VX can be decontaminated to below the detectable limit by spraying with OPAB solution if the spray time interval is greater than 24 minutes
- Attempts to analyze the sump liquid for residual agent were unsuccessful.

Based on the experimental results, further evaluation of the OPAB concept is suggested. However, because of possible degradation of OPAB concentrate, the subsequent experiments should utilize freshly prepared OPAB solution. A fresh source of 1-octyl pyridinium 4-aldoxime bromide is needed to do this.

9.0 CONCLUSIONS

A summary of the coupon decontamination results from the experimental concept evaluation is given in Table 17. Based on analysis of the results further evaluation of the following concepts is suggested:

TABLE 17. SUMMARY OF COUPON DECONTAMINATION RESULTS FROM THE FIVE EVALUATED CONCEPTS

Decontamination Method	Conditions	Residual Agent Remaining on Coupon following Decontamination		
		HD	GB	VX
Hot Gases	60 minutes at 150 C	BDL[a]	BDL	BDL
Steam	HD-40 minutes at 100 C GB-60 minutes at 100 C VX-180 minutes at 100 C	BDL	BDL	BDL
Vapor Circulation	HD-Heat up to 48C GB-Heat up to 48C VX-2 hours at 48C	BDL	BDL	96.4
Flashblast	48 kw applied power	BDL	99.6	99.5
OPAB	Spray 10 times at 1.5 to 3.0 liter/m^2 coverage	99.7	BDL	99.6

(a) BDL = Below detectable limit.

- Hot Gases
- Steam
- OPAB

Suggested starting conditions in the Steel/Concrete Tests (Subtask 6) for the Hot Gas and Steam concepts are given in Table 17. The OPAB concept will require further evaluation using stainless steel coupons in order to confirm that OPAB is capable of decontaminating stainless steel contaminated with HD or VX to below the detectable limit. Because the OPAB currently in storage may have degraded, any additional efforts should use a source of freshly prepared OPAB solution.

The Flashblast test results suggest that ventilation of the test chamber may cause agent volatilization. As such, ventilation tests are suggested in which coupons are spiked with agent and placed in the test chamber. The chamber would then be ventilated with nitrogen under a slightly reduced pressure. The exhaust from the chamber would then be passed through impingers. Following the experiment, the coupons and impinger will be analyzed for agent. The results of these experiments will also serve as a baseline for concepts employing circulating gases.

REFERENCES

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2) "Development of Novel Decontamination Techniques for Chemical Agents (GB, VX, HD) Contaminated Facilities", by H. M. Grotta et al., Volume II, AD-B073 034L, February, 1983.

3) "Test Report for Task 3, Subtask 3: "Chemical Concepts Preliminary Screening", by S.M. Tausheck et. al., (See Appendix II).

4) "Test Report for Task 3, Subtask 4: Diffusion Studies", by E.R. Zamejc, J. D. Underwood and E.J. Mezey, (See Appendix III).

APPENDIX V

SUBTASK 6. STEEL/CONCRETE TESTS

TEST REPORT

FOR

TASK 3 SUBTASK 6

STEEL/CONCRETE DECONTAMINATION TESTS

to

UNITED STATES ARMY
TOXIC AND HAZARDOUS MATERIALS AGENCY

by

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EXECUTIVE SUMMARY

Three decontamination concepts (steam, hot gas and OPAB) were evaluated for their effectiveness in removing agent from contaminated painted and unpainted mild and stainless steel surfaces, concrete and unglazed porcelain. Also, a comparison was made between the solvent extraction/gas chromatography method and the air sampling/enzyme inhibition method for agent surface analyses.

Results of the steam experiments suggest that the materials of interest can be decontaminated to below the detectable limit. Undecomposed agent can be volatilized from the contaminated surface during the process.

Results of the hot gas experiments suggest that the materials of interest can be decontaminated to below the detectable limit. Undecomposed agent can be volatilized from the contaminated surface during the process.

Results of the OPAB experiments suggest that painted and unpainted mild and stainless steel can be decontaminated to below the detectable limit. Over 99 percent of the HD spiked onto concrete and the GB spiked onto porcelain was decontaminated by OPAB. VX contaminated porcelain was decontaminated to below the detectable limit.

Thus, the steam and hot gas concept should be further evaluated in Subtask 7 for an engineering/economic analysis. Further evaluations of the OPAB concept should focus on specific applications such as decontamination of pipes, tanks and sumps and as a protective coating during application of the hot gas and steam concept.

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1.0 INTRODUCTION

As part of the systematic selection process for the most-promising agent decontamination concepts, five concepts (i.e., Hot Gases, Vapor Circulation, Steam, OPAB and Flashblast) were evaluated using unpainted 304 stainless steel contaminated with either HD, GB or VX as the test substrate.(1) Based on the results of these tests the following concepts were selected with USATHAMA's concensus for further experimental evaluations in the Subtask 6 Steel/Concrete tests.

- Hot Gases
- Steam
- OPAB (aqueous solution of 1-octylpyridinium 4-aldoxime bromide)

2.0 OBJECTIVE

The objective of this subtask was to evaluate three concepts for their decontamination effectiveness of painted and unpainted mild steel, painted stainless steel, and painted and unpainted concrete contaminated with HD, GB, or VX as the test substrates*.

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* Unglazed porcelain was substituted for concrete in the GB and VX tests. Painted concrete was not evaluated in the tests because of analytical interferences.

Results of Subtask 6 experiments are to be used to select the most promising concept(s) (i.e., those concept(s) which effectively decontaminated the test substrates) for an engineering/economic evaluation in Subtask 7.

3.0 APPROACH

A description of the decontamination test chamber, coupons and analytical procedures follows in the next section. The vapor sampling apparatus and test procedures are described in Section 7.0.

3.1 Test Chamber Description

A detailed description of the decontamination test chamber is given in Reference 1.

3.2 Coupon Description

The steel coupons used in the Subtask 6 tests consisted of either 14 gauge 304 stainless steel or 14 gauge mild steel. Each coupon measured 5 inches by 5 inches.

Painted mild steel and stainless steel coupons were prepared using the following procedure:

1. Coupons were cleaned in hexane.
2. Stainless steel coupons' surfaces were roughened with fine sandpaper in order to aid adherence of paint.
3. One coat of Krylon green primer No. 1346 (conforms to MIL-P-8585) was applied and allowed to dry for one to three hours.
4. Two coats of forest green alkyd paint, NSN-8010-00-111-7937 (conforms to MIL-E-52798A) were applied, allowing each coat to dry for 24 hours.
5. Painted coupons were allowed to cure under ambient conditions for at least two weeks prior to testing.

A description of the concrete coupons used in the HD decontamination tests is given as follows:

- Composed of a mortar mix (i.e., sand, cement and water). The preparation method is given in Reference 2.
- 1/4 inch thick by 5 inches square
- Porosity of about 12 percent
- Aged at ambient conditions for about 12 months.

A description of the unglazed porcelain coupons used in the GB and VX decontamination tests is given as follows.

- Source - American Olean Tile Co.
- 1/4 inch thick by 5 inches square
- Porosity of about 32.0 percent.

3.3 Coupon Spiking Method

3.3.1 Steel Coupons

Each coupon used in the steel decontamination tests was spiked with munition grade agent containing about 10 mg of HD, GB or VX. The agent was diluted with hexane to obtain concentrations of 1 mg VX/ml, 2 mg GB/ml or 10 mg HD/ml. Thus, in order to spike the coupon with 10 mg of agent, a total of 1 ml of dilute HD solution; 5 ml of dilute GB solution; or 10 ml of dilute VX solution was applied to each coupon.

Recovery tests were performed in which alkyd painted stainless steel and unpainted mild steel coupons were spiked with HD, GB, or VX using dilute agent solutions. The coupons were then extracted with hexane and the extractant analyzed for agent using established procedures[1]. The recovery efficiency (i.e., the amount of agent extracted divided by the amount of agent spiked) of agent from the steel coupons was then determined. The results of the recovery tests are given in Table 1.

The high recovery efficiencies shown in Table 1 demonstrated that spiking painted and unpainted steel coupons with dilute agent solutions

TABLE 1. RECOVERY EFFICIENCY OF HD, GB, AND VX FROM ALKYD PAINTED STAINLESS STEEL AND UNPAINTED MILD STEEL

Agent	Material	Recovery Efficiency	Average Recovery Efficiency
HD	UMS[a]	0.94 0.95	0.94
HD	PSS[b]	0.92 0.89	0.90
GB	UMS	0.96 0.95	0.95
GB	PSS	0.83 0.85 0.85	0.84
VX	UMS	0.93 1.00	0.96
VX	PSS	0.50 0.57 0.60	0.56

(a) Unpainted mild steel
(b) Painted stainless steel (Note: This recovery efficiency was used for decontamination efficiency calculations on both painted stainless steel and painted mild steel coupons).

was feasible. The average recovery efficiencies were used in subsequent analyses to calculate the decontamination efficiency as follows:

$$\text{Residual Agent on Decontaminated Coupon (mg)} = \frac{\text{Result of GC Analysis (mg)}}{\text{Recovery Efficiency}}$$

$$\text{Decontamination Efficiency (\%)} = \left(\frac{\text{10 mg - Residual Agent on Decontaminated Coupon}}{\text{10 mg}} \right) \text{X 100}$$

3.3.2 Concrete Coupons

Concrete coupons that were used in the HD decontamination tests were spiked with neat (i.e., undiluted agent) at a dose level of 1.8 mg HD/gm concrete. The coupons were spiked following mounting in the test chamber in order to minimize handling. The coupon spiking was performed with a 1000 μl syringe which allowed dosing the coupon with dispersed drops of agent that were quickly absorbed into the porous matrix.

The 1.8 mg HD/gm concrete spiking level was based on related studies.[3] To determine the volume of agent required for spiking, ten coupons were weighed and a mean weight of 210 gms was obtained. The volume of HD spiked onto each coupon ws then calculated as follows:

$$\frac{\text{Volume HD}(\mu\text{l})}{\text{coupon}} = \frac{\text{210 gms concrete/coupon x 1.8 mg HD/gm concrete}}{1.27\ \text{mg HD}/\mu\text{l}}$$

$$= 298\ \mu\text{l HD/coupon}$$

For the initial recovery efficiency tests, the coupons were spiked with HD and extracted with hexane. Hexane was the first choice as the extractant because of its use in the painted steel extraction tests and other studies.[3] Also, hexane does not extract agent interfering components from the alkyd paint used in this study. The results of the HD recovery tests using hexane are given in Table 2. Because the recovery efficiencies were lower than anticipated, the tests were repeated using methylene chloride

TABLE 2. RECOVERY EFFICIENCY OF HD FROM CONCRETE

Extractant	Exposure Time[a] min	Recovery Efficiency	Average Recovery Efficiency
Hexane	0	0.30	
	0	0.22	0.28
	0	0.33	
	1440	0.0075	
	1440	0.0010	0.0077
	1440	0.0145	
Methylene Chloride	0	0.57	
	0	0.59	0.59
	0	0.60	
	1440	0.12	
	1440	0.02	0.05
	1440	0.009	

(a) The exposure time is the period of time between spiking and extracting the coupon. This time does not include a 30 minute period required to crush the concrete coupons.[3]

as the extractant. The results of these tests indicate that methylene chloride is preferred over hexane to extract HD from concrete. Although a low recovery efficiency was observed, the recovery is such that at least a 99.8 percent decontamination efficiency would be observable:

- 378 mg HD (Spiking Level) x .01 (Worst case recovery in 24 hours) = 3.78 mg HD
- 3.78 mg x 150 mL extraction solvent = 25 μg/mL HD
- .05 μg/mL (Detection limit for HD)/25 μg/mL (Concentration of HD in extracts) = 0.2% Detection or 99.8% Decontamination Efficiency.

Sample concentration was used to increase the observable decontamination efficiency. For example, when the extraction solvent is concentrated to 10 ml, the observable decontamination efficiency is [0.05/(3.78x10 ml)] = 99.993 percent.

It is important to note that because methylene chloride is used as the extractant, the evaluation of painted concrete decontamination could not be performed because of extraction of interferences from the alkyd paint. However, tentative conclusions may still be reached upon comparison of the data from the painted steel decontamination tests with the unpainted concrete test data.

3.3.3 Unglazed Porcelain

Investigations into the fate of agent on concrete indicate that GB and VX are either decomposed or rendered unextractable by an interaction with concrete even after a relatively short exposure period (i.e., several hours).(3) As such, an alternative material (i.e., unglazed porcelain) was evaluated which was more inert to the agents and had similar properties (i.e., porosity) to concrete. The results of GB and VX recovery tests are described as follows.

A spiking level of 1.8 mg of neat GB or VX/gm of porcelain was selected for the recovery tests. At a mean weight of 215.6 gm/porcelain coupon*, the volume of agent spiked per coupon was:

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* Average weight of 10 coupons

$$\text{GB Volume} = 215.6 \text{ gm/coupon} \times 1.8 \text{ gm GB/gm} \div 1.09 \text{ mg/}\mu\text{l}$$
$$= 356\ \mu\text{l of neat GB}$$

$$\text{VX Volume} = 215.6 \text{ gm/coupon} \times 1.8 \text{ gm VX/gm} \div 1.0083 \text{ mg/}\mu\text{l}$$
$$= 385\ \mu\text{l of neat VX}$$

The initial test focused on the recovery of GB from intact (i.e., not crushed prior to extraction) coupons. The results of duplicate experiments revealed no measurable chromatographic peaks (i.e., recovery efficiency less than 0.01). The second test involved spiking with neat agent, crushing the porcelain, and extracting the pieces with either hexane or methylene chloride. The porcelain was crushed such that the pieces were capable of passing through a ₸24/40 ground glass joint (i.e., about 1/2 inch in diameter).

Results of the VX recovery tests given in Table 3 indicate that the use of methylene chloride as a solvent is preferred over hexane. An acceptable VX recovery of 22 percent was obtained after a 24 hour exposure period. With a detection limit of 5 µg VX/ml, this analytical method would be capable of determination of a 99 percent decontamination effectiveness. A higher decontamination effectiveness could be obtained if the extract is concentrated.

The GB recovery test results given in Table 3 indicate that less than one percent of the spiked GB is extractable after 1440 hours. The lower recovery of GB as compared with VX may be explained by the higher volatility of GB. It is important to note that GB decontamination tests using unglazed porcelain were still performed despite the low recovery in order to obtain information on diffusion of GB through the porous porcelain. In these tests the extract from the coupons were concentrated at least tenfold to confirm decontamination.

3.4 Analytical Methodology

The samples generated from an experiment which were quantitatively analyzed for agent included 1) painted and unpainted steel coupons, 2) con-

TABLE 3. RECOVERY EFFICIENCY OF GB AND VX FROM UNGLAZED PORCELAIN

Agent	Extractant	Exposure Time,[a] min	Recovery Efficiency	Average Recovery Efficiency
VX	Hexane	0	0.60	
		0	0.58	0.55
		0	0.46	
		1440	0.037	
		1440	<0.01	0.01
		1440	<0.01	
	Methylene Chloride	0	0.78	0.63
		0	0.47	
		1440	0.20	0.22
		1440	0.23	
GB	Methylene Chloride	0	0.21	0.18
		0	0.14	
		1440	<0.01	<0.01
		1440	<0.01	

a) The exposure time is the period of time between spiking and extracting the coupon. This time does not include a 30 minute period required to crush the porcelain coupon.

crete and unglazed porcelain coupons, 3) impinger solutions, 4) condensates and 5) chamber rinse solution. The following analytical procedures were used. Actual analytical data is given in Battelle Laboratory Record Book Nos. 39546 and 39876.

3.4.1 Steel Coupons

The steel coupons were individually extracted by immersion in 50 mls of hexane. Methylene chloride was not used for extraction because it also extracts paint components. The coupons were allowed to soak in the hexane for about 5 minutes. The hexane was collected and then concentrated to one ml using a Kuderna-Danish evaporative concentrator prior to analysis.

The concentrate was analyzed by either a Carlo Erba Gas Chromatograph equipped with a Flame Ionization Detection (FID) system or a Hewlett-Packard Gas Chromatograph equipped with a Flame Photometric Detection (FPD) system* and a Hewlett-Packard Autosampler. Both chromatographs were equipped with a 3[illegible] meter glass capillary column coated with SE-52 phase. Data handling and storage was accomplished with a Hewlett-Packard 1000 computer using Computer Imaging Inquiry Systems Inc. CALS (computer automated laboratory system) software.

Standard solutions containing known concentrations of agent (e.g., 10 ppm, 1 ppm, 0.1 ppm) were regularly used for preparation of calibration curves. The standards were analyzed at the same conditions as the samples. Analyses of the standard solutions indicated that the lower detection limit for all agents was about 0.1 μg/ml.

3.4.2 Concrete and Unglazed Porcelain Coupons

The concrete and unglazed porcelain coupons were crushed to pieces less than about 1/2 inch in cross-section. The pieces were passed through a ₸24/40 ground glass joint into an Erlenmeyer flask. 150 ml of methylene

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* Phosphorus mode for GB and VX, sulfur mode for HD.

chloride was then added and the mixture was then allowed to stand for 15 minutes. Methylene chloride rather than hexane was used because of its higher extraction efficiency (See Tables 2 and 3). During extraction, the mixture was periodically agitated. After about 15 minutes the methylene chloride was decanted from the solid. The decant was then concentrated and analyzed in the same method as described in Section 3.4.1.

3.4.3 Impingers

An impinger train was used to collect vaporized agent contained in the chamber exhaust stream from the hot gas concept tests. Exhaust gas was drawn through the impinger train at a rate of 25 to 40 liter/min. The impinger train consisted of 2-500 ml Greenberg-Smith impingers in series. 100 ml of ethylene glycol diacetate (EGDA) solution was placed in each impinger used during the HD experiments while 100 ml of pH 4.5 H_2SO_4/distilled water solution was placed in each impinger used during the GB and VX experiments.

Because agent may diffuse through the porous concrete or unglazed porcelain coupons during application of the steam and hot gases concept, the portion of the test chamber behind the coupons (i.e., opposite to the side of the coupon spiked with agent) was sampled during these experiments. Sampling entailed drawing a nitrogen bleed of 2 to 6 liter/min through the rear chamber and then through two 25 ml impingers in series. The 25 ml impingers each containing 10 ml of impinger solution were not used during the steel decontamination tests.

Following an experiment, the volume of each impinger was recorded. The solution was then stored at -5 C until analysis could be completed.

The EGDA used for the collection of HD was analyzed for the presence of HD by Gas Chromatography/Hall Detection. This procedure gave a detection limit of about 0.2 µg/ml. The EGDA was analyzed without prior concentration.

The 4.5 pH water was analyzed directly for the presence of VX and GB by an enzyme inhibition method using a Technicon Industrial System Autoanalyzer®. The enzymatic procedure for GB and VX gave a detection

limit of about 0.2 and 0.02 μg/ml, respectively. The 4.5 pH water was analyzed without concentration.

3.4.4 Condensate/Rinses

The condensate samples from the steam decontamination tests involving steel coupons were extracted in a two-liter separatory funnel. The condensate was loaded into the separatory funnel and washed with three separate 50 ml volumes of methylene chloride. The wash samples were combined and concentrated to one ml using the Kuderna-Danish appartus. The concentrate was then analyzed in the same method as the coupon extract.

The chamber rinse samples (isopropyl alcohol and/or hexane) were collected as required and concentrated to one ml using the Kuderna-Danish concentrator. The concentrate was then analyzed in the same method as the coupon extracts.

3.5 Test Procedures

The approaches used to implement the five decontamination concepts were outlined in a Test Plan (steel decontamination tests) and a SOP (concrete and unglazed porcelain decontamination tests).

4.0 HOT GAS DECONTAMINATION CONCEPT

The hot gas concept employs the use of heated gases such as burner exhaust gases to thermally decontaminate a building.[4] The purpose of the experiments described below was to determine the decontamination effectiveness of the hot gas concept by subjecting painted stainless steel, painted mild steel, unpainted mild steel, and porous (i.e., concrete and unglazed porcelain) test coupons contaminated with agent to a hot-gas composition near that of a combustion exhaust gas.

4.1 Description of Hot Gas Experiments

4.1.1 Hot Gas System

The hot gas system is described in detail in Reference 1. A slightly modified version was employed in the concrete and unglazed porcelain decontamination tests.

4.1.2 Test Procedure

Three coupons were placed in coupon holders and then each coupon was spiked with either 10 mg of agent using dilute agent solution (steel tests) or 1.8 mg agent per gram of coupon weight (concrete and unglazed porcelain tests). After spiking the chamber lid was secured. The hot gas flow was started and regulated during the experiment such that the coupons were heated to about 150 C*. to achieve this required maintaining the gas temperature inside the chamber at about 350 to 400 C. Once the coupons reached 150 C, the gas flow was regulated such that the coupons were maintained at 150 C for either zero, one or two hours. These times were based on previous results(1) which showed that maintaining unpainted stainless steel at 150 C for 60 minutes caused decontamination to below the detectable limit. After the required time at temperature was achieved, the hot gas flow was stopped and the chamber was allowed to cool overnight. The following day, the coupons were removed for analysis. The chamber was then rinsed with hexane which was also collected for analysis as required.

4.2 Discussion of Results from the Hot Gas Decontamination Experiments

The results from the hot gas experiments are discussed in the following section. Actual data obtained from the experiments are recorded in Battelle Laboratory Record Book No. 39524 and 39869. An example of

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* Measured on the back side of the coupon (i.e., the side opposite to the one spiked with agent).

the effect of the hot gas treatment on unpainted mild steel is given in Figure 1.

Table 4 gives a summary of the operating conditions for the steel decontamination hot gas experiments.

A summary of the coupon decontamination results from the nine steel decontamination hot gas experiments is shown in Table 5. Except for one painted mild steel coupon from Experiment 14, all coupons were decontaminated to below the detectable limit in each of the hot gas tests. The extractive analytical procedure indicated 0.6 μg of GB remained on this coupon. (Detection Limit = 0.1 μg GB). However, the vapor sampling procedure (See Section 7.4) on the second painted mild steel coupon indicated that less than 0.03 μg of GB remained on the coupon. As such, it is probable that the GB detected by the extractive procedure was a false positive.

A summary of the coupon decontamination results from the concrete and unglazed porcelain decontamination tests is given in Table 6. The results indicate that HD contaminated concrete and GB or VX contaminated unglazed porcelain can be decontaminated to below the detection limit by heating to a temperature of 150 C.

Previous data[1] indicated that volatilization of undecomposed agent from contaminated unpainted stainless steel coupons occurs during hot gas decontamination. Steel decontamination test impinger and water trap analyses (See Table 7), indicate the hot gas exhaust stream also contains undecomposed agent when decontaminating painted and unpainted steel coupons. In the case of HD, a relatively large fraction of the HD spiked on the coupons was recovered in the impingers (20.8 mg of HD was recovered in Experiment 10 out of 30 mg spiked).

Impinger analyses from impinger samples taken during the hot gas decontamination of concrete and unglazed porcelain experiments are given in Table 8. As in the steel decontamination tests, large quantities of agent were contained in the exhaust stream from the chamber. Analyses of impingers used to sample the rear portion of the test chamber indicate

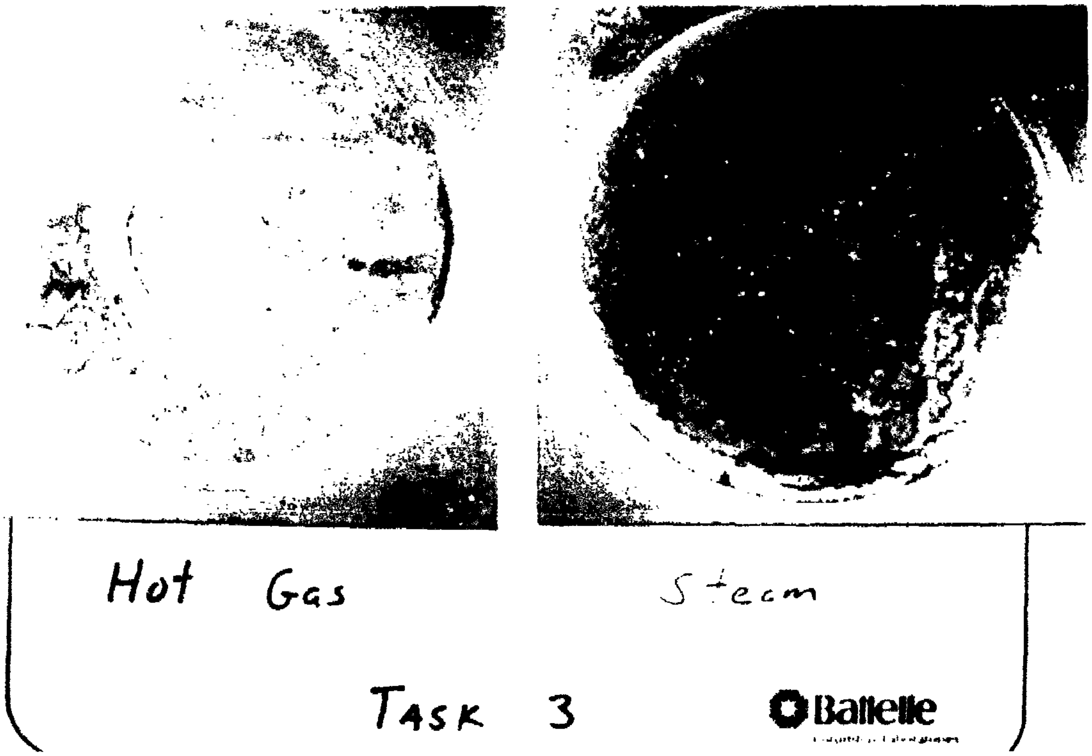

FIGURE 1. THE EFFECT OF THE HOT GAS AND STEAM DECONTAMINATION TREATMENTS ON UNPAINTED MILD STEEL

TABLE 4. SUMMARY OF CONDITIONS FOR THE DECONTAMINATION OF STEELS WITH HOT GAS

Hot Gas Experiment Number	Agent	Coupon Temperature Reached (C)	Time to Reach Temperature (Min)	Time at Temperature (Min)	CO_2[a] Flow Rate (nM^3/hr)	N_2[a] Flow Rate (nM^3/hr)	H_2O[b] Flow Rate (nM^3/hr)	Total Flow into System (nM^3/hr)	Chamber Pressure (mmHg)
7	HD	150	101	120	0.28	2.07	0.57	2.92	-1.5
8	VX	150	115	120	0.28	2.07	0.57	2.92	-0.9
9	GB	150	112	120	0.28	2.01	0.54	2.80	-0.4
10	HD	150	105	60	0.28	1.98	0.54	2.80	-4.7
11	GB	150	106	60	0.28	1.95	0.54	2.78	-2.4
12	VX	150	90	60	0.28	1.98	0.54	2.78	-2.8
13	HD	150	105	60	0.40	2.24	0.82	3.46	0.0
14	GB	150	135	60	0.37	2.12	ND [c]	ND	-2.8
15	VX	150	135	60	0.37	2.15	ND	ND	-8.2

a) Corrected for inlet pressure

b) Calculated from the vapor pressure of water at the water heater temperature, the furnace inlet pressure and the CO_2 and N_2 flow rates.

c) Not determined.

TABLE 5. RESULTS FROM HOT GAS DECONTAMINATION EXPERIMENTS - GB, VX AND HD SPIKED PAINTED AND UNPAINTED STEEL

Hot Gas Experiment Number	Agent	Coupon Type[(a)]	Time at Temperature[(b)], min.	Residual Agent on Coupons, mg	Decontamination Efficiency, percent
7	HD	PMS	120	<0.0011	>99.99
		PSS	120	<0.0011	>99.99
		UMS	120	<0.0011	>99.99
8	GB	PMS	120	<0.0001	>99.999
		PSS	120	<0.0001	>99.999
		UMS	120	<0.0001	>99.999
9	VX	PMS	120	<0.0002	>99.998
		PSS	120	<0.0002	>99.998
		UMS	120	<0.0001	>99.999
10	HD	PMS	60	<0.0011	>99.99
		PSS	60	<0.0011	>99.99
		UMS	60	<0.0011	>99.99
11	GB	PMS	60	<0.0001	>99.999
		PSS	60	<0.0001	>99.999
		UMS	60	<0.0001	>99.999
12	VX	PMS	60	<0.0002	>99.998
		PSS	60	<0.0002	>99.998
		UMS	60	<0.0001	>99.999
13	HD	PSS	60	<0.0013	>99.99
		PMS	60	(c)	-
		UMS	60	(c)	-
14	GB	PMS	60	0.0006	99.994
		PMS	60	(c)	-
		UMS	60	(c)	-
15	VX	PMS	60	<0.0002	>99.998
		PMS	60	(c)	-
		UMS	60	(c)	-

(a) PMS = alkyd painted mild steel
PSS = alkyd painted stainless steel
UMS = unpainted mild steel

(b) At a coupon temperature of about 150 C.

(c) Sample analyzed by Vapor Sampling Method (see Section 7.0).

TABLE 6. RESULTS FROM HOT GAS DECONTAMINATION EXPERIMENTS - HD SPIKED CONCRETE AND GB, VX SPIKED UNGLAZED PORCELAIN

Hot Gas Experiment Number	Agent	Coupon Type	Agent Spiked per Coupon, mg	Time at Temperature,[a] min	Average Residual Agent on Coupons,[c] mg	Decontamination Efficiency Percent
16	HD	Concrete	378	60	<0.02	>99.99
17	GB	Porcelain	388	60	<0.02	>99.99
18	VX	Porcelain	388	60	<0.06	>99.98
19	HD	Concrete	378	0[b]	<0.02	>99.99
20	GB	Porcelain	388	0[b]	<0.05	>99.98
21	VX	Porcelain	388	0[b]	<0.1	>99.97

a) At a coupon temperature of 150 C.

b) Coupons brought to a temperature of 150 C and then cooldown was initiated.

c) Incorporates a one percent agent recovery efficiency (see Tables 2 and 3).

TABLE 7. AGENT VOLATILIZATION DURING THE HOT GAS DECONTAMINATION EXPERIMENTS LISTED IN TABLE 5

Hot Gas Experiment Number	Agent	Agent Found in Impingers (mg)	Agent Found in Water Trap (mg)	Agent Found in Chamber Rinse (mg)	Total Agent Volatilized[b] (mg)
7	HD	<0.079	<0.001	0.175	0.175
8	GB	ND[a]	ND	ND	ND
9	VX	ND	<0.0003	<0.0004	ND
10	HD	20	<0.001	<0.001	20
11	GB	0.014	0.102	<0.0001	0.242
12	VX	0.2	0.0002	0.019	0.219
13	HD	ND	ND	ND	ND
14	GB	ND	ND	ND	ND
15	VX	ND	ND	ND	ND

(a) ND = not determined.
(b) Spiked quantities = 10 mg per coupon X 3 coupons per experiment = 30 mg.

TABLE 8. AGENT VOLATILIZATION/DIFFUSION DURING THE HOT GAS DECONTAMINATION EXPERIMENTS LISTED IN TABLE 6.

Hot Gas Experiment Number	Agent	Coupon Type	Agent Found in Hot Gas Exhaust Stream Impingers[a], mg	Agent Found in Rear Chamber Bleed Stream[b], mg
16	HD	Concrete	0.48	0.04
17	GB	Porcelain	11[c] 1.9[d]	1.2
18	VX	Porcelain	0.099[c] 0.097[d]	0.172
19	HD	Concrete	23.8[c]	< 0.01
20	GB	Porcelain	96[c] 14.4[d]	12
21	VX	Porcelain	0.152[c] 0.124[d]	0.260

a) The 100 ml of impinger liquid contained in each of the two 500 ml impingers in series was combined for analysis.

b) The 10 ml of impinger liquid contained in each of the two 25 ml impingers in series was combined for analysis.

c) Impingers in place from the start of the experiment up to the time the back temperature of the coupon reached 93 C.

d) Impingers in place from the time the back temperature of the coupon reached 93 C to the end of the experiment.

that agent either diffused through the porous coupon or around the gasket material located between the coupon holder and the test chamber.

It is important to note that operation at higher gas temperatures may not completely eliminate volatilization because volatilization appears to occur primarily during the heatup stage. Also, operation at higher temperatures would require additional fuel requirements and increase the damage to the building due to overheating. Thus, a method must be developed to remove/destroy volatilized agent contained in the exhaust gas when decontaminating a building in the field. Also, a method must be developed to limit and/or block the diffusion of agent through porous materials.

4.3 Hot Gas Concept Conclusions/Recommendations

Tentative conclusions based on evaluation of the data from the hot gas experiments are as follows:

- Painted and unpainted mild and stainless steel contaminated with HD, GB, or VX can be decontaminated to below the detectable limit by maintaining the surface at a temperature of 150 C for 60 minutes.
- Porous materials contaminated with either HD (concrete), GB (porcelain), or VX (porcelain) can be decontaminated to below the detectable limit by maintaining the material at a temperature of 150 c throughout for 60 minutes.
- Because undecomposed agent volatilizes from the contaminated material, a method to decompose agent contained in hot gas may be required to prevent emissions of agent or redeposition in "cold" spots.

Based on the experimental results, further evaluation of the hot gas concept in the engineering/economic analysis is recommended. Maintaining a temperature of 150 C for 60 minutes is suggested as a basis for the engineering/economic analysis.

5.0 STEAM DECONTAMINATION CONCEPT

The steam concept employs the use of ambient pressure steam to decontaminate a building by either chemical hydrolysis and/or physical removal (e.g., solubilization or evaporation) of agent contaminants.[4] Steam may be applied either manually or remotely (i.e., injecting steam into a sealed building). The purpose of the experiments described below was to determine the decontamination effectiveness of steam by subjecting painted stainless steel, painted and unpainted mild steel, concrete and unglazed porcelain test coupons contaminated with agent to steam.

5.1 Description of Steam Experiments

5.1.1 Steam System

The steam system used in the steel decontamination tests is described in detail in Reference 1. A slightly modified version was employed in the concrete and unglazed porcelain decontamination tests.

5.1.2 Test Procedure

Three coupons were placed in coupon holders and then each coupon was spiked with either 10 mg of agent using dilute agent solution (steel tests) or 1.8 mg agent per gram of coupon weight (concrete and unglazed porcelain tests). The chamber lid was then secured and the steam flow was started.

As steam condensed on the coupons, the coupons were heated from ambient temperature (about 25 C) to a temperature near the boiling point of water. In the initial set of experiments, steam flow was then maintained for an additional 40 minutes when HD was the contaminant; 60 minutes when GB was the contaminant; or 130 minutes when VX was the contaminant. These operation times were based on previous results.[1] Subsequent operation times were based on the results from the initial set of decontamination experiments. After the required time at temperature was achieved, the steam flow was stopped and the chamber was allowed to cool overnight.

The following day, the coupons were removed for analysis. The chamber was then rinsed with hexane which was also collected for analysis as required.

5.2 Discussion of Results from the Steam Decontamination Experiments

The results of the steam experiments are discussed in the following section. Actual data obtained from the experiments are given in Battelle Laboratory Record Book No. 39524 and 39869. An example of the effect of the steam treatment on unpainted mild steel is given in Figure 1.

Table 9 gives a summary of the operating conditions for the steam experiments. The average steam flow for the eleven steel decontamination experiments corresponds to a flow of about 17.7 kg of steam/m^3/hr for the 0.07 cubic meter chamber. Application of the steam concept to decontamination of field structures will require a lower steam flow rate per unit volume which, consequently, will require operation for a longer period than that shown in Table 9 because of longer heatup times. However, the time the painted and unpainted steel surfaces are maintained at about 100 C should correspond to the times shown in Table 9.

A summary of the coupon decontamination results from the eleven steel decontamination experiments are shown in Table 10. T results indicate that all coupons were decontaminated to below the detectab limit in the steam experiments except the painted stainless steel coup in Experiments 7 (HD) and 11 (VX). HD contaminated stainless steel coupons re decontaminated to below the detectable limit when the time at temperature was increased from 40 minutes (Experiment 7) to 60 minutes (Experiments 10 and 14). A repeat of Experiment 11 indicated that VX contaminated painted stainless steel (See Experiment 13) can be decontaminated to below the detectable limit at the same conditions (i.e., time at temperature).

A summary of the coupon decontamination results from the concrete and unglazed porcelain decontamination tests is given in Table 11. The results indicate that HD contaminated concrete and GB contaminated unglazed porcelain can be decontaminated to below the detection limit by maintaining

TABLE 9. SUMMARY OF CONDITIONS FOR THE DECONTAMINATION OF STEELS WITH STEAM

Steam Experiment Number	Agent	Time to Reach Temp.[a] (min)	Time at Temp. (min)	Total Experiment Time (min)	Total Condensate Collected(ml)	Steam Flow Rate (kg/hr)
7	HD	25	40	65	1740	1.61
8	GB	55	60	115	2345	1.22
9	VX	25	180	205	4940	1.45
10	HD	35	60	95	2340	1.48
11	VX	40	240	280	6420	1.37
12	GB	40	60	100	1920	1.15
13	VX	20	240	260	3100	0.71
14	HD	23	60	83	1700	1.23
15	GB	38	60	98	2690	1.64
16	HD	30	60	90	1960	1.31
17	VX	31	240	271	2220	0.48

a) Time for coupons to reach about 100 C (boiling point of water)

TABLE 10. RESULTS FROM STEAM DECONTAMINATION EXPERIMENTS - GB, VX AND HD SPIKED PAINTED AND UNPAINTED STEEL

Steam Experiment Number	Agent	Coupon Type[(a)]	Time at Temperature[(b)], min.	Residual Agent on Coupons, mg	Decontamination Efficiency, percent
7	HD	PMS	40	<0.0011	>99.99
		PSS	40	0.012	99.9
		UMS	40	<0.0011	>99.99
8	GB	PMS	60	<0.006	>99.94
		PSS	60	<0.006	>99.94
		UMS	60	<0.005	>99.95
9	VX[(c)]	PMS	180	<0.0002	>99.998
		PSS	180	<0.0002	>99.998
		UMS	180	<0.0001	>99.999
10	HD	PMS	60	<0.0011	>99.99
		PSS	60	<0.0011	>99.99
		UMS	60	<0.0011	>99.99
11	VX[(c)]	PMS	240	<0.0002	>99.998
		PSS	240	0.0004	99.996
		UMS	240	<0.0001	>99.999
12	GB	PMS	60	<0.0001	>99.999
		PSS	60	<0.0001	>99.999
		UMS	60	<0.0001	>99.999
13	VX	PMS	240	<0.0002	>99.998
		PSS	240	<0.0002	>99.998
		UMS	240	<0.0001	>99.999
14	HD	PSS	60	<0.0011	>99.99
		PSS	60	<0.0011	>99.99
		PSS	60	<0.0011	>99.99
15	GB	PSS	60	<0.0001	>99.999
		PSS	60	(d)	-
		UMS	60	(d)	-
16	HD	PMS	60	<0.0011	>99.99
		PMS	60	(d)	-
		UMS	60	(d)	-
17	VX	PMS	240	0.0002	99.998
		PMS	240	(d)	-
		UMS	240	(d)	-

(a) PMS = alkyd painted mild steel
PSS = alkyd painted stainless steel
UMS = unpainted mild steel

(b) At a coupon temperature of about 100 C.

(c) Analysis of the coupon samples by GC-FID showed detectable quantities of a compound(s) with a retention time similar to VX. Analysis by capillary column GC-FPD indicated much lower concentrations of VX (see table above). The GC-FPD showed another phosphorus containing compound which interfered with VX determination by the GC-FID.

(d) Sample analyzed by vapor sampling method (see Section 7.0).

TABLE 11. RESULTS FROM STEAM DECONTAMINATION EXPERIMENTS - HD SPIKED CONCRETE AND GB, VX SPIKED UNGLAZED PORCELAIN

Steam Steam Experiment Number	Agent	Coupon Type	Agent Agent Spiked per Coupon, mg	Time at Time at Temperature,[a] mg	Average Residual Agent on Coupons,[b] mg	Decontamination Efficiency, Percent
18	HD	Concrete	378	60	<0.02	>99.99
19	GB	Porcelain	388	60	<0.02	>99.99
20	VX	Porcelain	388	240	<0.02	>99.99
21	HD	Concrete	378	60	<0.02 [c]	>99.99[c]
22	GB	Porcelain	388	60	<0.02	>99.99
23	VX	Porcelain	388	240	<0.02	>99.99

(a) At a coupon temperature of about 100 C.

(b) Incorporates a one percent agent recovery efficiency (see Tables 2 and 3).

(c) Samples contained compounds that may interfere with the quantitative analysis. An elevated baseline was observed in the chromatogram, but no peaks were observed above this baseline.

contact with steam for one hour after a temperature of at least 100 C is attained throughout the material. VX contaminated unglazed porcelain requires up to a four hour steam contact time following attainment of 100 to cause decontamination to below the detection limit.

Decontamination of the coupons involved not only destruction of agent, but also physical removal of agent. In the steam experiments, agent can be physically removed from the coupons by either volatilization and/or washed off by steam condensation. Results from the analysis of the sump condensates shown in Table 12 substantiate that agent wash-off does occur. Because the sump condensate contains undecomposed agent, the condensate would require a subsequent treatment. The method can entail recycle of exhausted steam and condensate to the steam generator. Repeated recycle should provide sufficient contact time of undecomposed agent with steam to ensure complete destruction. For example, the condensate can be collected in a sump, pumped from the building to temporary storage tanks, and recycled to the steam generator. The cycle could be repeated until no agent is detected in the condensate.

Tests were conducted to determine if condensate containing undecomposed agent can be decontaminated by reboiling the condensate. Condensate samples from steam Experiments No. 8 (GB), No. 9 (VX) and No. 10 (HD) were boiled and the steam condensed. The condensate was collected and analyzed for a residual agent. Results indicate that no agent was present in the condensates. As such, recycle of the sump condensate through the boiler during decontamination of facilities should cause destruction of residual agent.

A minor amount of VX was found in the chamber rinse in Experiment 9. The source of the agent is probably attributed to residual agent in the condensate collection system. The condensate reboil experiments suggest that continued operation of the steam concept should cause decontamination of the condensate pipes. An alternative would be to pump a liquid decontaminant such as OPAB solution through the pipes following steam decontamination.

Analyses of impingers used to sample the rear portion of the test chamber are given in Table 13. The results suggest agent diffusion through porous materials may not occur during implementation of the steam concept. However, further substantiating tests are required.

TABLE 12. AGENT VOLATILIZATION DURING THE STEAM DECONTAMINATION EXPERIMENTS LISTED IN TABLE 10

Steam Experiment Number	Agent	Agent Found in Condensate (mg)	Agent Found in Chamber Rinse (mg)	Total Agent Volatilized (mg)
7	HD	0.117	<0.001	0.117
8	GB	0.0006	<0.0005	0.0006
9	VX	0.130	0.034	0.164
10	HD	ND[a]	<0.001	ND
11	VX	ND	<0.001	ND
12	GB	ND	ND	ND
13	VX	ND	ND	ND
14	HD	ND	ND	ND
15	GB	ND	ND	ND
16	HD	ND	ND	ND
17	VX	ND	ND	ND

(a) ND = not determined

TABLE 13. AGENT DIFFUSION DURING THE STEAM DECONTAMINATION EXPERIMENTS LISTED IN TABLE 11

Steam Experiment Number	Agent	Coupon Type	Agent Found in Impingers, mg
18	HD	Concrete	<0.065
19	GB	Porcelain	89 (a)
20	VX	Porcelain	<0.25
21	HD	Concrete	<0.1
22	GB	Porcelain	<60
23	VX	Porcelain	<25

(a) Steam condensate was noted in the impingers during the experiment. This indicates that steam, which may have contained intact agent, had flowed around the coupon (i.e., either between the coupon and gasket or between the coupon holder and gasket).

5.3 Steam Concept Conclusions/Recommendations

Tentative conclusions based on evaluation of the data from the steam experiments are as follows:

- Painted and unpainted mild and stainless steel contaminated with HD, GB, or VX can be decontaminated to below the detectable limit by maintaining the steel surface at a temperature near the boiling point of water for 60, 60, or 240 minutes, respectively.
- Porous materials contaminated with either HD (concrete) GB (porcelain) or VX (porcelain) can be decontaminated to below the detectable limit by maintaining the material at a temperature near the boiling point of water for 60, 60, and 240 minutes respectively.
- Steam decontamination includes the physical removal of undecomposed agent from the coupon by volatilization and wash-off. Thus, a method to remove/decompose agent contained in the exhausted steam and condensate from a building must be defined.

Based on the experimental results, further evaluation of the steam concept in the engineering/economic analysis is recommended. The suggested conditions for the engineering/economic analysis are as follows:

GB	-	60	minutes at a coupon temperature of about 100 C
HD	-	60	minutes at a coupon temperature of about 100 C
VX	-	240	minutes at a coupon temperature of about 100 C.

6.0 OPAB DECONTAMINATION CONCEPT

The OPAB concept involves decontamination by spray application of an aqueous solution of 1-octyl-pyridinium 4-aldoxime bromide (OPAB), OPAB* has the following chemical structure:

* A one kg supply of OPAB (denoted as BCL-OPAB) was synthesized[5] in a related project for use in Subtask 6 tests. The OPAB used in previous decontamination tests[1] was obtained from Battelle-Frankfurt.

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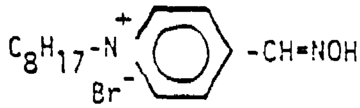


The selection of OPAB for experimental evaluation was based on studies performed at Battelle-Frankfurt (sponsored by the German Defense Ministry) which indicated OPAB to be highly effective in decontaminating VX. Previous tests at Battelle-Columbus[1] demonstrated the effectiveness of OPAB in decontaminating unpainted stainless steel contaminated with GB, HD, or VX. The purpose of the experiments described below was to determine the decontamination effectiveness of OPAB on painted stainless steel, painted and unpainted mild steel coupons when applied in the form of a spray.

6.1 Description of OPAB Experiments

6.1.1 OPAB Application System

The OPAB application apparatus is described in detail in Reference 1.

6.1.2 Test Procedure

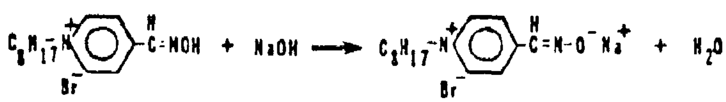
Three coupons were placed in coupon holders and then each coupon was spiked with either 10 mg of agent using dilute agent solution (steel tests) or 1.8 mg agent per gram of coupon weight (concrete and unglazed porcelain tests). The chamber lid was then secured. The spray application was initiated and repeated for a specified number of times at the desired time interval.

Following completion of the sprayings, the coupons were removed from the chamber and the chamber was rinsed with isopropyl alcohol followed by hexane. Liquid collected in the sump of the test chamber was stored for a sufficient period (i.e., overnight) to allow decontamination of undecomposed agent which may have been physically removed from the coupons by the action of the spray prior to analysis (as required).

6.2 Discussion of Results from the OPAB Decontamination Experiments

The results of the OPAB experiments are discussed in the following section. Actual data obtained from the experiments are recorded in Battelle Laboratory Record Book Nos. 39524 and 39869.

Results from the OPAB experiments using HD, GB, and VX contaminated steels are given in Tables 14, 15 and 16, respectively. These tests used OPAB which was synthesized under an ARO-STAS program[5] in support of this work. The OPAB in solid form was dissolved in water prior to each experiment to form a 5-weight-percent solution. For OPAB Experiments 18 and 19 (VX), a 5-weight-percent solution of the sodium salt of OPAB was used. The sodium salt of OPAB was prepared by the following reaction:



Results of the HD/steel decontamination tests given in Table 14 indicate that the activity of OPAB for destruction of HD appears to be related to the solution formulation. The BCL-OPAB formulation (neat OPAB dissolved in water) is slightly acidic (pH 4 to 5) whereas the OPAB formulation used in previous, less successful HD decontamination tests[1] (using the sodium salt of OPAB and additives dissolved in water) is basic (pH 9 to 10). The slightly acidic OPAB formulation appears to be more reactive with HD than the basic OPAB formulation.

Results of the GB and VX decontamination tests given in Table 15 and 16, respectively indicate that the slightly acidic OPAB formulation (BCL-OPAB) is an effective decontaminant for GB and VX. The basic OPAB (BF-OPAB) formulation appears to be slightly less effective on VX.

A summary of the coupon decontamination results from the concrete and unglazed porcelain decontamination tests is given in Table 17. Residual agent values were obtained using the GC/FPD method on coupon extracts (no concentration) and the GC/MS method on concentrated coupon extracts. The use of GC/FPD on the concentrated coupon extracts was not possible because

TABLE 14. RESULTS FROM HD/STEEL DECONTAMINATION EXPERIMENTS USING BCL-OPAB SPRAY

OPAB Experiment Number	Spray Interval, (a) min.	Number of Sprays	Coupon (b) Type	Residual Agent on Coupon, mg.	Decontamination Efficiency, (c) percent	Agent Found in Rinse, mg.	Agent Found in Sump, mg.
9	30	10	USS	<0.0001	>99.99	<0.0001	<0.0001
			UMS	<0.0001	>99.99		
			PMS	<0.0001	>99.99		
11	30	10	USS	<0.0001	>99.99	<0.0001	<0.0001
			UMS	<0.0001	>99.99		
			PSS	<0.0001	>99.99		
13	20	15	PSS	<0.0002	>99.99	0.0001	<0.0001
			PSS	0.035	99.7		
			PMS	0.024	99.8		
15	20	15	PMS	0.004	99.96	N.A. (e)	N.A.
			PMS	(d)	--		
			UMS	(d)	--		

(a) Coverage, nozzle type, supply pressure based on diffusion studies and held constant for all experiments.

(b) PMS = Painted mild steel, PSS = Painted stainless steel, UMS = Unpainted mild steel, USS = Unpainted stainless steel.

(c) The decontamination efficiency is the percent removal/destruction of agent from the coupon surface. Based on 10 mg of agent spiked on each of three coupons used in each test, the decontamination efficiency is given by:

$$\text{Decontamination Efficiency (\%)} = \left[\frac{10\text{ mg} - \text{Average Residual Agent on Coupons}}{10\text{ mg}}\right] \times 100$$

(d) For vapor sampling tests. (See Section 7.0)

(e) Not analyzed.

TABLE 15. RESULTS FROM GB/STEEL DECONTAMINATION EXPERIMENTS USING BCL/OPAB SPRAY

OPAB Experiment Number	Spray Interval,[a] min.	Number of Sprays	Coupon[b] Type	Residual Agent on Coupon, mg.	Decontamination Efficiency,[c] percent	Agent Found in Rinse, mg.	Agent Found in Sump, mg.
8	30	10	UMS	0.0003	99.99		
			PMS	0.0004	99.99	0.0001	0.0012
			PSS	<0.0001	>99.99		
10	20	15	UMS	<0.0001	>99.99		
			PMS	<0.0001	>99.99	<0.0001	0.0001
			PSS	0.0002	99.99		
16	20	15	PMS	0.060	99.4		
			PMS	(d)	--	N.A.[e]	N.A.
			UMS	(d)	--		

(a) Coverage, nozzle type, supply pressure based on diffusion studies and held constant for all experiments.

(b) PMS = Painted mild steel, PSS = Painted stainless steel, UMS = Unpainted mild steel, USS = Unpainted stainless steel.

(c) The decontamination efficiency is the percent removal/destruction of agent from the coupon surface. Based on 10 mg of agent spiked on each of three coupons used in each test, the decontamination efficiency is given by:

$$\text{Decontamination Efficiency (\%)} = \left[\frac{10\text{ mg} - \text{Average Residual Agent on Coupons}}{10\text{ mg}}\right] \times 100$$

(d) For vapor sampling tests. (See Section 7.0)

(e) Not analyzed.

TABLE 16. RESULTS FROM VX/STEEL DECONTAMINATION EXPERIMENTS USING BCL-OPAB SPRAY

OPAB Experiment Number	Spray Interval,[a] min.	Number of Sprays	Coupon Type[b]	Residual Agent on Coupon, mg.	Decontamination Efficiency,[c] percent	Agent Found in Rinse, mg.	Agent Found in Sump, mg.
7	30	10	USS UMS PMS	<0.0002 0.0006 0.0047	>99.99 99.99 99.95	0.0025	0.023
12	20	15	USS UMS PSS	<0.0002 <0.0002 0.0014	>99.99 >99.99 99.99	<0.0001	0.0008
14	15	20	PMS PSS UMS	0.002 0.002 0.010	99.98 99.98 99.9	0.0002	0.0004
17	20	15	PMS PMS UMS	<0.002 (e) (e)	-- -- --	N.A.[d]	N.A.
18[f]	30	10	UMS PMS PSS	0.003 0.138 0.040	99.97 98.6 99.6	0.113	0.001
19[f]	30	10	UMS PMS PSS	0.002 0.031 0.009	99.98 99.7 99.91	0.003	0.0008

(a) Coverage, nozzle type, supply pressure based on diffusion studies and held constant for all experiments.

(b) PMS = Painted mild steel, PSS = Painted stainless steel, UMS = Unpainted mild steel, USS - Unpainted stainless steel.

(c) The decontamination efficiency is the percent removal/destruction of agent from the coupon surface. Based on 10 mg of agent spiked on each of three coupons used in each test, the decontamination efficiency is given by:

$$\text{Decontamination Efficiency (\%)} = \left[\frac{10\text{ mg} - \text{Average Residual Agent on Coupons}}{10\text{ mg}}\right] \times 100$$

(d) For vapor sampling tests.

(e) Not analyzed

(f) OPAB experiments 18 and 19 utilized the sodium salt of OPAB dissolved in water. OPAB Experiments 7 through 17 utilized neat OPAB dissolved in water.

TABLE 17. RESULTS FROM OPAB DECONTAMINATION EXPERIMENTS - HD SPIKED CONCRETE AND GB, VX SPIKED UNGLAZED PORCELAIN

OPAB Experiment Number	Agent	Coupon Type	Agent Spiked per coupon, mg	Spray Interval, minutes	Number of Sprays	Average Residual Agent on Coupons by GC/FPD,(a)(c) mg	Average Residual Agent on Coupons by GC/MS,(b)(c) mg	Decontamination Efficiency, percent
20	HD	Concrete	378	7.5	40	<3.0	>0.1	99 to 99.97
21	GB	Porcelain	388	7.5	40	<3.0	>0.1	99 to 99.97
22	VX	Porcelain	388	7.5	40	<3.0	<0.1	>99.97
23	HD	Concrete	378	7.5	40	<3.0		>99
24	GB	Porcelain	388	7.5	40	<3.0	--	>99
25	VX	Porcelain	388	7.5	40	<3.0	--	>99

(a) Analysis of coupon extract without concentration.

(b) Analysis of coupon extract following concentration from 150 ml to 1 ml.

(c) Reported values assume a worst case of one percent recovery efficiency. Actual recovery efficiencies may be higher. See Sections 3.3.2 and 3.3.3.

either residual OPAB and/or OPAB/agent decomposition products extracted from the coupon did not volatilize during concentration. The resultant concentrate was a viscous liquid with the color of OPAB. Analysis by GC/FPD resulted in an elevated baseline which prevented quantification of agent. Analysis of selected concentrated coupon extracts by GC/MS indicated residual HD and GB remained following OPAB decontamination. However, no residual VX was detected by GC/MS in the unglazed porcelain concentrated extract. A possible cause for the incomplete decontamination of the HD and GB contaminated porous coupons is that OPAB, because of its molecular size, did not penetrate as far into the coupon pores as the smaller HD and GB molecules. VX on the other hand which is similar in molecular size to OPAB was decontaminated to below the detectable limit. Observations on the concrete and porcelain coupons following the OPAB decontamination tests indicated that liquid had completely penetrated through the 1/4-inch thick coupons. However, the OPAB did not diffuse with the liquid but remained within about 1/16-inch of the surface sprayed.

Because of probable limitations in the depth of penetration of OPAB into porous materials, further evaluations of OPAB as a general facility decontaminant are not recommended. However, selective uses for OPAB such as decontamination of painted and unpainted steels and as a protective coating should be considered.

6.3 OPAB Concept Conclusions/Recommendations

Tentative conclusions based on evaluation of the data from the OPAB experiments are as follows:

- HD contaminated painted and unpainted mild and stainless steels can be decontaminated by spraying with the slightly acidic OPAB solution every 30 minutes for 5 hours (Total amount applied = about 15 to 30 liters/m^2).
- GB and VX contaminated painted and unpainted mild and stainless steels can be decontaminated by spraying with the slightly acidic OPAB solution every 20 minutes

for 5 hours (Total amount applied = about 25 to 45 liters/m^2.

- VX contaminated unglazed porcelain can be decontaminated by spraying with the slightly acidic OPAB solution every 7.5 minutes for 5 hours (Total amount applied = about 80 liters/m^2). At the same conditions, HD contaminated concrete and GB contaminated porcelain were not completely decontaminated.
- The use of OPAB for decontamination of porous materials beyond a penetration depth of about 1/16 inch is not recommended. However, further evaluation on specific applications for OPAB should be performed.

7.0 VAPOR SAMPLING TESTS

In support of this program, an extraction analytical method was developed[6] for the determination of agent on painted and unpainted mild and stainless steel (see Section 3.4). In contrast, current USATHAMA analytical protocol for sampling of contaminated agent materials/structures involves the use of an air-sampling method rather than an extraction method. The air-sampling method entails sampling the head space over a possible contaminated or chemically decontaminated surface by drawing a known volume of air at a known rate through bubblers. For example, for GB and VX the bubblers contain liquid such as dilute sulfuric acid which traps agent. Following sampling, the liquid is analyzed for agent by, for example, an enzymatic technique. The results of the air-sampling analyses are used to determine whether the specific agent was present in the atmosphere at concentrations greater than the Time Weighted Average (TWA). The TWA levels are as follows:

- HD = 3×10^{-3} mg/m^3 [5]
- GB = 1×10^{-4} mg/m^3 [6]
- VX = 1×10^{-5} mg/m^3 [6]

If these TWA levels are not surpassed after a decontamination procedure then the item can be classified as being in a 3X condition.[7][8]

7.1 Approach

The objective of the vapor sampling tests was to determine the vapor concentration of agent over decontaminated coupons. The hot gas (hot gas Experiments 13-15), steam (steam Experiments 15-17) and OPAB (OPAB Experiments 15-17) concepts were used to generate decontaminated coupons for the vapor sampling tests. The selection of conditions for the decontamination tests was based on the analysis of extracts from previous tests which indicated that the coupons were decontaminated to near or below the detectable limit.

In each decontamination test, three mild steel coupons (one unpainted and two painted) were spiked with 10 mg of HD, GB or VX and the decontamination treatment was applied. Following the treatment, one of the painted mild steel coupon was analyzed for residual agent using the extraction method. The second painted mild steel coupon and the unpainted mild steel coupon were subjected to the vapor sampling tests. The coupons were stored in sealed bags at -5 C until the vapor sampling tests could be completed.* Analysis of two painted steel coupons subjected to identical decontamination conditions using two different analytical procedures (i.e., by extraction and by vapor sampling) allows a comparison between the methods to be made.

In the vapor sampling experiments, air heated to 60 C was passed over and around a coupon also heated to 60 C. Heated air rather than ambient temperature air was used to enhance the evaporation of any residual agent from the coupon. A higher temperature was not selected because of the potential for thermal decomposition of the agents. Residual agent released to the air was collected and analyzed.

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* The storage period at -5C ranged from about 10 weeks for the hot gas and steam decontaminated coupons to about one week for the OPAB decontaminated coupons.

7.2 Description of Vapor Sampling Experiments

7.2.1 Test Apparatus

The vapor sampling apparatus is illustrated in Figures 2 and 3. A chamber was constructed as shown in Figure 2 to hold one coupon for vapor sampling. The chamber was equipped with two coupon supports, a baffle, a thermocouple, an inlet pipe and an outlet pipe. The coupon supports allowed circulation of air underneath the coupon while the baffle diverted the air entering the chamber around the coupon. In order to monitor coupon temperature, a thermocouple was placed in contact with the coupon surface. The chamber was selaed with a gasketed Gore-Tex®.

Heating of the chamber and inlet air was provided by the use of heating tapes. Temperature was controlled/monitored with temperature controllers. A vacuum pump was used to maintain the chamber at a negative pressure (about minus 1 inches of water). The flow rate of air was controlled by a rotameter as shown in Figure 3. A dry gas test meter was used to measure total flow of air passing through the impingers.

Two impingers in series were used to trap residual agent vapor when the contaminants are GB or HD. Ethylene glycol diacetate or pH 3.7 water were used in the impinger for trapping HD or GB and VX, respectively.

7.2.2 Test Procedures

One test coupon was placed in the vapor sampling chamber, the lid attached and the vapor sampling chamber heated to 60 C. Air, heated to 60 C was then directed through the vapor sampling chamber to impingers. An air flow rate of about one liter/min was used in the GB and VX tests while an air flow rate of 6 liters/min was used in the HD tests. The air flow was continued for the desired sampling time and then the impingers were removed for analysis. The liquid from the impingers was refrigerated until analysis was completed. After the impingers were removed, a fresh set of impingers were installed and the second sampling period initiated. Following two sampling periods, the test chamber and tubing between the chamber and collection system were rinsed with hexane.

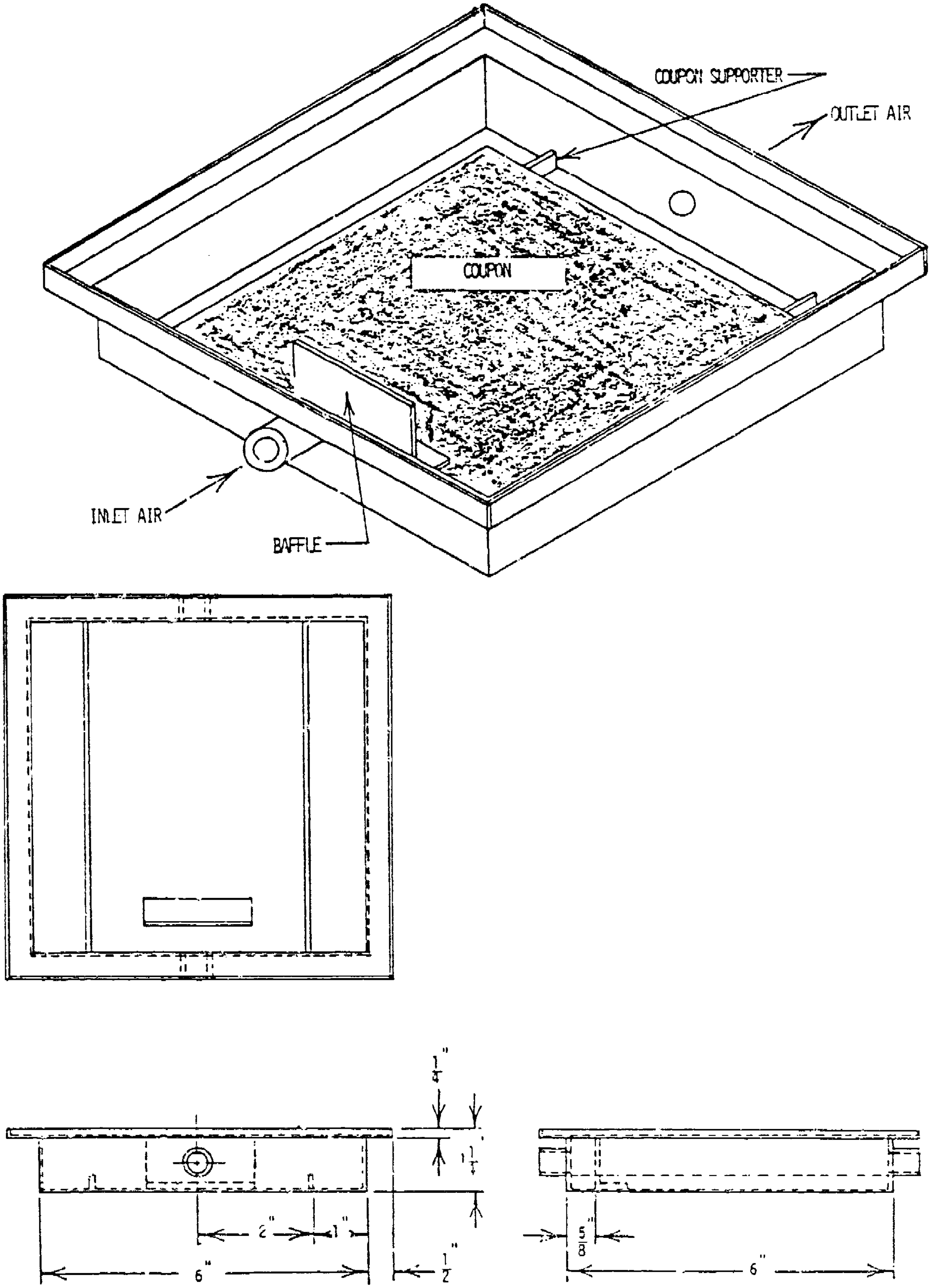

FIGURE 2. VAPOR SAMPLING TEST CHAMBER

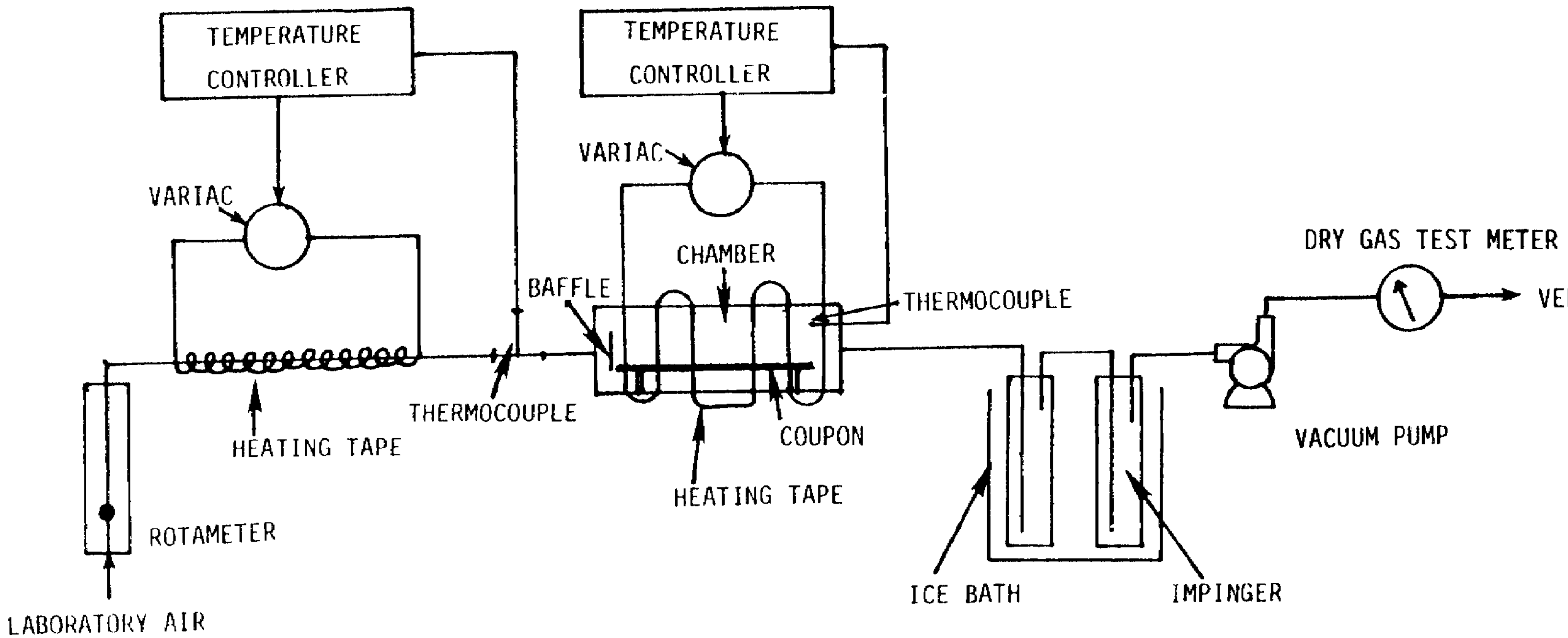

FIGURE 3. VAPOR SAMPLING SYSTEM (GB, HD AND VX)

7.2.3 Analytical Procedures

The EGDA from the impingers used during the HD experiments was analyzed for HD by Gas Chromatography (GC)/Hall detection. The pH 3.7 water from the impingers used during the GB and VX experiments was analyzed for GB and VX using an enzyme inhibition method (see Section 3.4.2). In both cases, the solution was analyzed without concentration.

7.3 Discussion of Results from the Vapor Sampling Experiments

7.3.1 Baseline Tests

Prior to conducting vapor sampling tests with decontaminated coupons, baseline tests were performed. The baseline tests determined 1) the collection efficiency of each agent (HD, GB and VX) by the vapor sampling technique and 2) the duration of the sampling periods.

The collection efficiency was determined by comparing the amount of agent collected from the sampling system with the amount of initially agent spiked on the coupon.

Results from the baseline experiments are given in Table 18. The results indicate that although complete recovery of agent was not achieved, the detectable agent air concentrations were near the TWA levels for GB and VX. The detectable air concentration was well above the TWA level for HD because of the lower sensitivity of the GC/Hall Detector analytical procedure as compared with the enzymatic method.

In the baseline experiments, a two hour sampling period was employed for each impinger set. The results of the baseline experiments indicate that agent was detected in the second 2-hour sampling period in the case of GB and VX. Because no HD was detected in the second 2-hour sampling period, vapor sampling of the decontaminated coupons was performed using two sets of impingers with each used for a one hour sampling period. Two sets of impingers and a two-hour sampling period was used for decontaminated coupons initially contaminated with GB or VX.

TABLE 18. RESULTS FROM VAPOR SAMPLING BASELINE EXPERIMENTS

			1st Impinger Set		2nd Impinger Set			
Agent	Coupon[a] Type	Agent Spiked μg	Agent Found, μg	Agent Air[b] Concentration, μg/m3	Agent Found, μg	Agent Air[b] Concentration, μg/m3	Detectable[c] Agent Concentration, μg/m3	TWA μg/m3
HD	UMS	10,000	2622	22,034	<22	<184	184	3
HD	PMS	10,000	2935	24,664	<19	<160	160	3
HD	UMS	200	51	142	19.4	54	54	3
HD	PMS	200	27	84	-	-	52	3
GB	UMS	100	0.113	0.82	0.293	2.19	0.15	0.1
GB	PMS	100	0.506	3.67	0.106	0.86	0.16	0.1
VX	UMS	20	0.18	0.14	0.007	0.05	0.03	0.01
VX	PMS	20	0.007	0.05	0.008	0.06	0.03	0.01

(a) UMS = Unpainted mild steel, PMS = Painted mild steel.

(b) Agent air concentration ($\mu g/m^3$) = agent found (μg)/volume of air sampled (m^3).

(c) Detectable air concentration ($\mu g/m^3$) = Detection limit of instrument ($\mu g/ml$) x Impinger volume (ml)/ volume of air sampled (m^3).

7.3.2 Vapor Sampling of Decontaminated Coupons

Results from the vapor sampling of decontaminated coupons are given in Table 19. All HD-contaminated coupons for which analyses are available were decontaminated to below the detectable limit of the vapor sampling method by either the hot gas, steam, or OPAB concepts. GB-contaminated coupons were decontaminated to below the detectable limit by only the hot gas concept. Positive responses to the enzyme inhibition analytical procedure were obtained from impingers used in the steam/UMS, OPAB/UMS, and OPAB/PMS vapor sampling experiments. Because of the lack of selectivity of the enzymatic procedure, the positive responses may be caused by decomposition products or other contaminants (e.g., the decontaminant) which may exhibit cholinesterase activity.*

Positive responses were also obtained for all of the VX-contaminated coupons except the steam/PMS coupon. Again, a positive response indicates that the coupon may have had residual VX contamination. However, a negative response suggests that the coupon did not have residual VX contamination unless VX decomposition products were formed which reacted with the color producing chemical in the enzymatic procedure (i.e. 5,5'-dithiobis-2-nitrobenzoic acid). This may lead to a false negative because the color produced above may counteract the absence of color caused by VX interaction with the bovine enzyme.

A comparison of results from the vapor sampling and extraction methods is given in Table 20. Analysis of coupons from the GB/hot gas and VX/steam experiments gave anomalous results in that the extraction method involving a GC-FPD for agent detection gave a positive response while the vapor sampling procedure involving the more sensitive enzyme inhibition apparatus gave negative results. However, analysis of the coupons from the VX/hot gas and VX/OPAB experiments gave a positive response for VX by the vapor sampling/enzymatic procedure and a negative response for VX by the extraction/GC-FPD procedure. The positive responses by the enzymatic method were below the detection limit of the GC-FPD method.

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* NaOH, hexane, and organic solvents interfere with the enzymatic procedure but do not necessarily cause cholinesterase depression.

TABLE 19. RESULTS FROM VAPOR SAMPLING EXPERIMENTS INVOLVING DECONTAMINATED COUPONS

Decontamination Method	Agent	Coupon Type[a]	1st Impinger Set: Agent Found, µg	1st Impinger Set: Agent Air Concentration,[b] µg/m³	2nd Impinger Set: Agent Found, µg	2nd Impinger Set: Agent Air Concentration,[b] µg/m³	Detection Limit,[c] µg/m³	Equivalent TWA, µg/m³
Hot Gas	HD	UMS	<19.8	BDL[d]	<19.4	BDL	89	3
Hot Gas	HD	PMS	<19.7	BDL	<21.0	BDL	128	3
Hot Gas	GB	UMS	<0.04	BDL	<0.04	BDL	0.25	0.1
Hot Gas	GB	PMS	<0.03	BDL	<0.03	BDL	0.21	0.1
Hot Gas	VX	UMS	0.504	1.35	0.380	0.96	0.01	0.01
Hot Gas	VX	PMS	0.004	0.02	0.004	0.02	0.02	0.01
Steam	HD	UMS	(e)	(e)	(e)	(e)	(e)	3
Steam	HD	PMS	<19.0	BDL	<20.0	BDL	94	3
Steam	GB	UMS	<0.03	BDL	0.08	0.76	0.21	0.1
Steam	GB	PMS	<0.02	BDL	<0.02	BDL	0.12	0.1
Steam	VX	UMS	0.007	0.04	0.006	0.04	0.01	0.01
Steam	VX	PMS	<0.002	BDL	<0.002	BDL	0.003	0.01
OPAB	HD	UMS	<11.5	BDL	<13.7	BDL	52	3
OPAB	HD	PMS	<10.5	BDL	<11.5	BDL	62	3
OPAB	GB	UMS	0.041	0.31	0.070	0.53	0.17	0.1
OPAB	GB	PMS	1.24	8.55	0.153	1.13	0.17	0.1
OPAB	VX	UMS	0.004	0.03	<0.002	BDL	0.02	0.01
OPAB	VX	PMS	0.015	0.11	<0.002	BDL	0.02	0.01

(a) UMS - Unpainted mild steel, PMS = Painted mild steel.

(b) Agent air concentration ($\mu g/m^3$) = agent found (μg)/volume of air sampled (m^3).

(c) Detection limit ($\mu g/m^3$) = Detection limit of instrument ($\mu g/ml$) x Impinger volume (ml)/volume of air sampled (m^3).

(d) BDL = Below detectable limit.

(e) Sample could not be analyzed because pH 3.7 water instead of EGDA was used in the impingers.

TABLE 20. COMPARISON OF THE VAPOR SAMPLING AND THE EXTRACTION METHODS FOR QUANTIFICATION OF HD, GB, AND VX ON PAINTED MILD STEEL COUPONS

Decontamination Method	Agent	Agent Found by Vapor Sampling,[a] μg	Agent Found by Extraction,[b] μg
Hot Gases	HD	<19.9	<1.2
	GB	< 0.03	0.6
	VX	0.008	<0.1
Steam	HD	<19.5	<1.2
	GB	< 0.02	<0.1
	VX	< 0.002	0.2
OPAB	HD	<11.0	4.0
	GB	1.393	60.0
	VX	0.015	<2.0

(a) GB and VX impingers analyzed by enzymatic inhibition. HD impingers analyzed by GC-Hall Detector.

(b) HD, GB, and VX coupon extracts analyzed by GC-FPD in either the phophorous mode (GB and VX) or the sulfur mode (HD).

Conclusions from the vapor sampling tests are as follows:

- Based on the baseline experiments for the elevated temperature vapor sampling technique, it appears that solvents such as hexane and methylene chloride are more effective than warm (60 C) air in extraction of HD, GB and VX from painted and unpainted metal surfaces.
- The solvent extraction method provides a more reliable determination of the presence of agent than the vapor sampling method due to the specificity of the GC detectors to the various agents and, occassionally, agent degradation products.

8.0 VENTILATION TESTS

Ventilation tests were performed to develop baseline data for the decontamination test chamber to show the effect of chamber ventilation on spiked coupons. No decontamination treatment was applied to the coupons during the ventilation tests. In the ventilation tests each coupon was spiked with 10 mg of agent and placed inside the decontamination test chamber. The test chamber was then ventilated by passing through nitrogen at ambient temperatures. The coupons were then removed and analyzed for agent. The results shown in Table 21 indicate that HD and GB are retained by paint but readily volatilize from unpainted steel. Impinger analyses indicated that undecomposed agent was volatilized from the coupons. A substantial amount of HD and VX were recovered by the impinger in Experiment 4 and 8, respectively.

9.0 CONCLUSIONS/RECOMMENDATIONS

Results from the decontamination tests indicate that the hot gas, and steam concepts are each effective decontaminants for painted and unpainted mild and stainless steel and porous materials such as concrete and unglazed porcelain. As such, these concepts should be further evaluated in the engineering/economic analysis. Further evaluations of OPA3

TABLE 21. RESULTS FROM CHAMBER VENTILATION (BASELINE) EXPERIMENTS USING ALKYD PAINTED AND UNPAINTED MILD AND STAINLESS STEEL COUPONS

Baseline Experiment Number	Agent	Ventilation Duration (a) (hrs)	Coupon Materials(b)	Residual Agent on Coupons(f) (mg)	Agent Found in Impinger (mg)	Agent Found in Rinse Solution (mg)	Total Agent Volatilized (mg)
1	GB	18	USS	< 0.006(c)	0.000015	<0.005	0.000015
2	HD	1	USS	< 0.0012(c)	< 0.001	< 0.00001	< 0.001
3	GB	1	USS	< 0.006(c)	0.001	< 0.005	0.001
4	HD	1	UMS PMS PSS	< 0.0001 2.12 2.48	8.2	0.004	8.204
5	GB	1	UMS PMS PSS	< 0.006 9.2 4.8	< 0.001	< 0.0004	< 0.001
6	GB	1	USS UMS USS	0.142 0.061 0.0001(d)	< 0.0001	< 0.0001	< 0.0001
7	HD	1	USS USS UMS	10.9 10.9 0.005(d)	< 0.021	< 0.0001	< 0.021
8	VX	1	USS UMS USS	(e) (e) (d)(e)	1.54	0.0014	1.5414
9	VX	1	PSS PMS USS	(e) (e) (d)(e)	0.040	0.001	0.041

(a) Ventilation flow rate = 0.28 nM^3/hr

(b) USS = Unpainted Stainless Steel
UMS = Unpainted Mild Steel
PSS = Painted Stainless Steel
PMS = Painted Mild Steel

(c) Average of three coupons

(d) Blank (i.e., unspiked coupon).

(e) Not analyzed

(f) Each coupon spiked with 10 mg of agent.

should focus on specific applications such as decontamination of painted and unpainted mild and stainless steel and as a protective coating on porous materials such as concrete.

Results from the vapor sampling tests indicate that the solvent extraction method works as well as or better than the vapor sampling method for quantification or HD, GB and VX on painted and unpainted steels. Future tests should consider the use of the solvent extraction method in conjunction with or as a replacement for the current Army vapor sampling procedures.

REFERENCES

(1) "Test Report for Task 3 Subtask 5: Stainless Steel Surface Decontamination Screening" by E.R. Zamejc et. al., (See Appendix IV).

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(5) "Organic Synthesis of Octyl Pyridinium 4-Aldoxime Bromide (OPAB)", by R.E. Wyant et. al., June 26, 1984, Contract ARO STAS TCN-84-273.

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(7) "Safety Regulations for Chemical Agents H, HD, and HT", DARCOM-R 385-31, para 5-1a, c, April, 1984.

(8) "Safety Regulations for Chemical Agents GB and VX", DARCOM-R 385-102, para. 5-1a, c, May 6, 1982.

APPENDIX VI

SUBTASK 7. ENGINEERING/ECONOMIC ANALYSIS

SUMMARY REPORT

for

TASK 3 SUBTASK 7

ENGINEERING/ECONOMIC ANALYSES

Contract DAAK11-81-C-0101

by

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EXECUTIVE SUMMARY

An engineering/economic analysis was performed on the hot gas and steam decontamination concepts selected from the experimental evaluations in Subtask 6. Equipment was specified and costs were estimated for application of the concepts to a model facility representative of structures observed during the Phase 1 site surveys. Results of the analyses suggest that it is feasible to apply the hot gas and steam contamination concepts for decontamination of field structures. In terms of cost, the hot gas concept is slightly preferred over the steam concept for the assumption that the entire building is contaminated throughout. In the hot gas concept, flue gases from the combustion of oil or natural gas are directed into a sealed and insulated building. Gas exhausted from the building is treated in an afterburner to destroy traces of volatilized agent, cooled by quenching with water, directed through an induced draft fan, and exhausted to the outside from a stack. The induced draft fan maintains both a flow through the system and a slight negative pressure within the building to minimize leakage of air potentially contaminated with agent to the outside.

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SUMMARY REPORT

FOR

TASK 3 SUBTASK 7

ENGINERING/ECONOMIC ANALYSES

Contract No. DAAK11-81-C-0101

to

UNITED STATES ARMY
TOXIC AND HAZARDOUS MATERIALS AGENCY

1.0 INTRODUCTION

As part of the development of novel decontamination concepts for chemical agent contaminated facilities an engineering/economic analysis was performed on the most promising decontamination concepts identified from the experimental evaluations in Subtasks 3 through 6[1-4]. The two concepts selected for the analyses are:

- Hot Gas
- Steam.

The engineering and economic feasibilities for the application of these concepts were determined with a "model" facility based on structures representative of those observed in the field. Heat and mass transfer calculations on the structure were used as the basis for process layouts, equipment selection and estimation of capital and operating costs. Because a certified procedure is not available, the following operations were not included in the cost analysis:

- Identification of contamination levels prior to decontamination
- Sampling and analysis during decontamination
- Verification of the effectiveness of the decontamination treatment.

Because these operations would be common to all decontamination methods, no effect on the comparison cost analysis is anticipated. An absolute building decontamination cost estimate cannot be made until further information is obtained in Phase III of the program.

2.0 OBJECTIVE

The objectives of Subtask 7 were to (1) determine the engineering feasibility of the most promising decontamination concepts as applied to structures representative of a field facility, (2) specify equipment and operations such that estimates of capital and operating costs can be made and (3) select a concept for further evaluation in Phase III.

3.0 DESCRIPTION OF FACILITY USED AS THE BASIS FOR THE ENGINEERING/ECONOMIC ANALYSES

Site surveys at agent-contaminated facilities were performed during Phase I of the program.(5) Based on these surveys, three structures were selected to serve as the basis for the engineering/economic analysis. A description of these structures is given in Table 1. Illustrations are given in Figures 1 through 3. Because data regarding the extent of contamination of field structures is unavailable, it was assumed that the buildings were contaminated throughout. Because of the limited penetration into porous material, OPAB was not selected for evaluation in the engineering/economic analysis.

4.0 HOT GAS DECONTAMINATION CONCEPT

The hot gas decontamination concept involves the use of combustion flue gas to thermally decontaminate materials such as steels and concrete. The conditions for decontamination and constraints in the process that were determined through experimental evaluation in Subtasks 5(3) and 6(4) are as follows.

- Painted and unpainted metal and stainless steel contaminated with HD, GB or VX can be decontaminated to below the detectable limit by maintaining the surface at a temperature of 150 C (300 F) for 60 minutes.

TABLE 1. DESCRIPTION OF THREE BUILDINGS USED AS THE BASIS FOR THE ENGINEERING ANALYSIS

Building Number	Model	Length, ft	Width, ft	Height, ft	Number of Floors	Description[a]
1	Building 412 at RMA[b]	150	70	15	1	One foot thick concrete basement with wood superstructure[c] (see Figure 1).
2	Building 1501 at RMA[b]	80	40	20[d]	3	Two foot thick reinforced concrete walls, one foot thick concrete floor and ceiling (see Figure 2).
3	Building 1640 at RMA[b]	100	50	20	1	18 gauge metal wall/ceiling structure with a one-foot thick concrete floor (see Figure 3).

(a) Each building contains 10 tons of steel (painted and unpainted) in the form of equipment, pipes, etc.
(b) RMA = Rocky Mountain Arsenal
(c) It is assumed that the wood superstructure is removed and incinerated in a hazardous waste incinerator leaving the concrete basement requiring decontamination.
(d) Height of each floor.

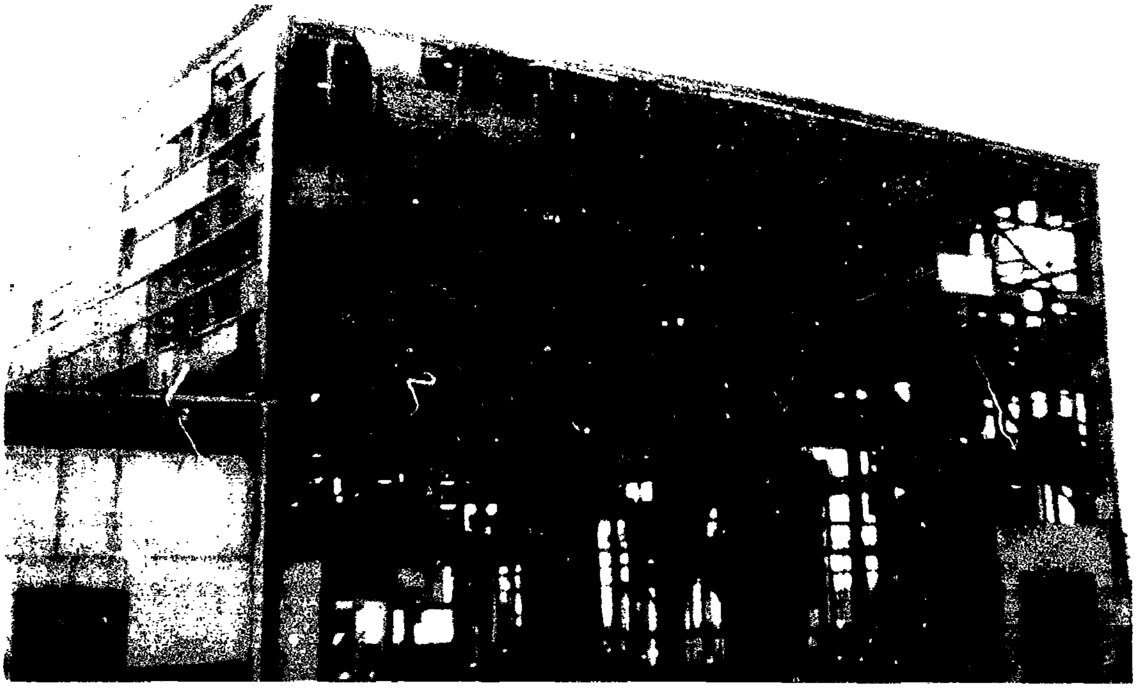


FIGURE 1. MODEL FOR BUILDING 1 OF THE FACILITY USED AS THE BASIS FOR THE ENGINEERING ANALYSIS

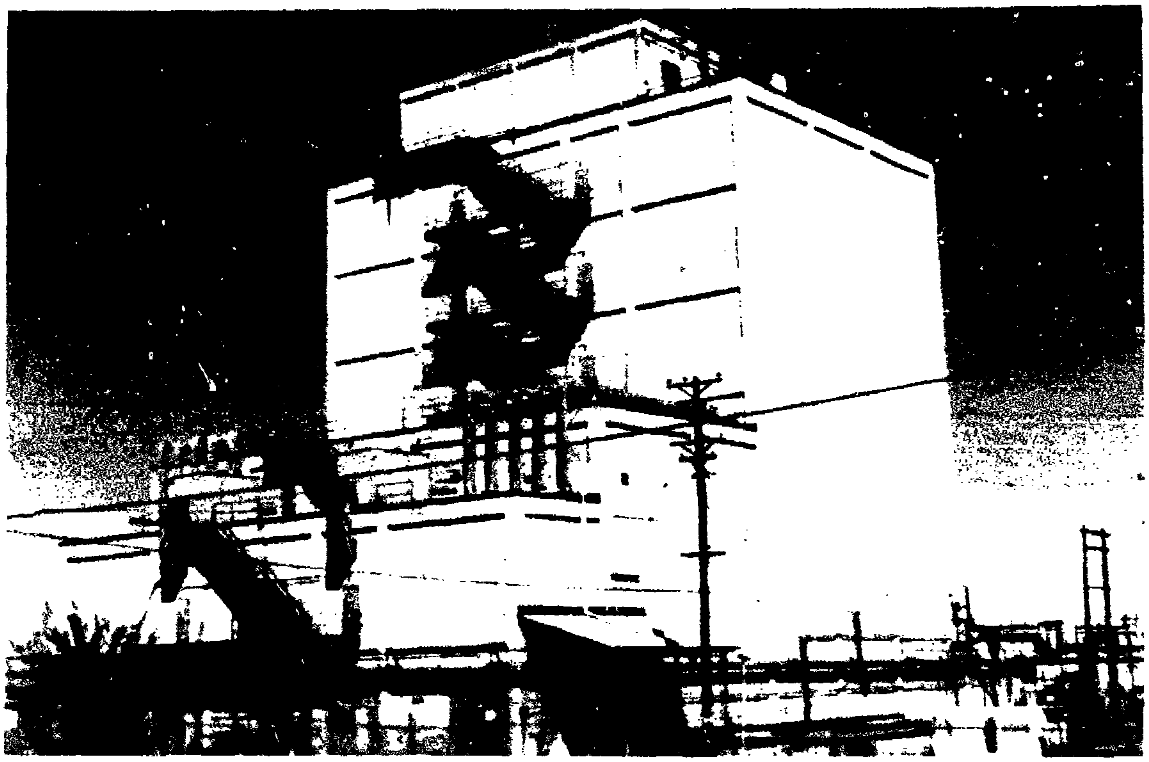


FIGURE 2. MODEL FOR BUILDING 2 OF THE FACILITY USED AS THE BASIS FOR THE ENGINEERING ANALYSIS

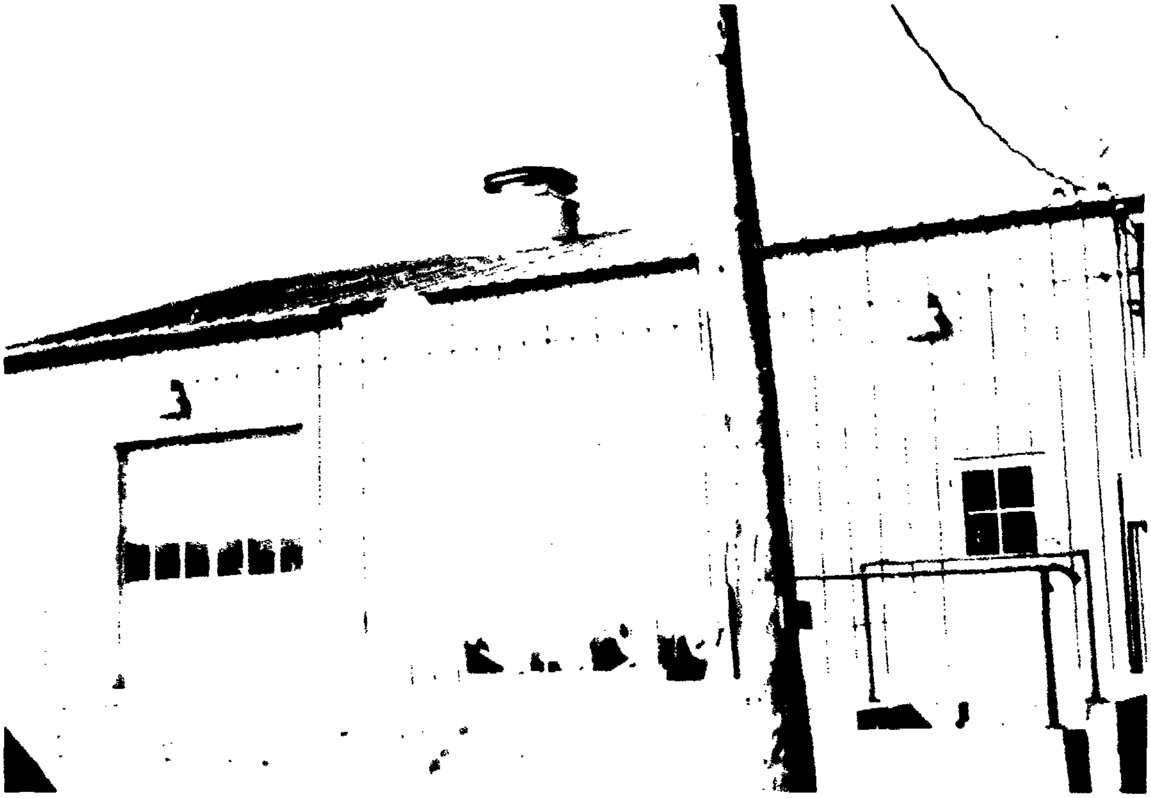


FIGURE 3. MODEL FOR BUILDING 3 OF THE FACILITY USED AS THE BASIS FOR THE ENGINEERING ANALYSIS

- Concrete contaminated with HD and porous materials (e.g., unglazed porcelain) contaminated with GB and VX can be decontaminated to below the detectable limit by heating the material up to a temperature of 150 C (300 F).
- Decontamination involves not only thermal degradation of agent but also volatilization of undecomposed agent from the material. The volatilized agent is expelled in the exhaust stream. Experimental results also suggest that agent may diffuse through porous materials from region of high temperatures to regions of lower temperatures. As such, methods to decompose volatilized agent and to prevent redeposition in "cold" spots are required.

These process conditions/constraints were used to perform heat balances and to specify and cost of the decontamination equipment.

4.1 Hot Gas Heat Transfer Calculations

Heat balances were performed on each of the three representative agent contaminated structures described in Table 1. In the heat balances the hot gas flow rate, inlet gas temperature and insulation thickness were varied to evaluate their effect on the feasibility and cost of the concept. The range of values used for the variables are as follows.

- Hot gas flow rate-1000, 2000, 3000 and 4000 scfm
- Inlet gas temperature-1500 and 2000 F
- Insulation thickness-2, 4 and 12 inches*

A description of the calculation procedure, including a sample calculation, and the results of the calculations are given in the next sections.

---

* An insulation thickness of 0 inches was evaluated but did not allow the requirement of heating all building materials throughout to a temperature of 300 F.

4.1.1 Hot Gas Heat Transfer Calculation Procedure

The method used to calculate heat requirements and times for each of the buildings involved an iterative method. The following are the steps in the calculation procedure:

Step 1: The hot gas outlet temperature (TOUT) is estimated.

Step 2: The inside heat transfer coefficient (HI) is calculated.

Step 3: The inside wall temperature (TW1) is calculated.

Step 4: The temperature profiles in the concrete walls and/or floor are calculated.

Step 5: A heat balance is performed where the heat released by the gas is compared with the heat absorbed by the concrete and the heat losses. Steps 1 through 4 are repeated until a heat balance is achieved.

Step 6: Steps 1 through 5 are repeated for the next time increment.

An example of the calculations using the Building 1 parameters given in Table 1 (i.e., H=15 ft, L=150 ft, W=70 ft) and a 2000 scfm hot gas flow at a 2000 F inlet gas temperature is given as follows. Definitions of the variables used in the calculations are given in Table 2.

4.1.1.1 Preliminary Calculations.

AREA1 = (150x70)+(150x15)x2 + (70x15)x2 = 17100 ft^2

AREA2 = 150x70 = 10500 ft^2

CSAREA = 70x15 = 1050 ft^2

HYDD = 4xCSAREA/PERIMETER = 4x1050/(140 + 30) = 24.7 ft

4.1.1.2 Step 1. In the first approximation TEMP1 = 70 F. Assume TOUT increases by 50 F in the first time interval of one hour.

TOUT = TEMP1 + 50 = 70 + 50 = 120 F

TABLE 2. DEFINITIONS OF VARIABLES USED IN THE BUILDING HEAT TRANSFER CALCULATIONS

ALPHA = Thermal diffusivity of concrete = CCON/(CPCON X DENSC)
AREA1 = Building surface area exposed to soil (ft^2)
AREA2 = Building surface area exposed to air (ft^2)
BIOT = Biot Number
CCON = Thermal conductivity of concrete = .7 BTU/ft/hr/F
CINS = Thermal conductivity of insulation = .05 BTU/ft/hr/F
CMASS = Mass of concrete in the building (lb)
CONG = Thermal conductivity of the hot gas (BTU/ft/hr/F)
CP = Specific heat of the hot gas (BTU/lb/F)
CPCON = Specific heat of concrete = .21 BTU/lb/F
CPINS = Specific heat of insulation = 0.2 BTU/lb/F
CPMET = Specific heat of the metal = 0.11 BTU/lb/F
CPSOIL = Specific Heat of soil = .44 BTU/lb/F
CSAREA = Cross Sectional area of hot gas flow (ft^2)
CSOIL = Thermal conductivity of soil = .3 BTU/ft/hr/F
DENS = Density of the hot gas (lb/ft/sec)
DENSC = Density of concrete = 144 lb/ft^3
DENSSL = Density of soil = 128 lb/ft^3
DEPTH = Concrete thickness (ft)
DINS = Insulation thickness = 0.167, 0.333 or 1.000 ft
FINF = Infiltration air flowrate = 100 SCFM
FLOW = Hot Gas flow rate = 1000, 2000, 3000, or 4000 SCFM
GR = Grashof number
H = Height of building (ft)
HCOND = Conduction heat transfer from the hot gas (BTU/ft/hr/F)
HFCON = Forced convection heat transfer from the hot gas ($BTU/ft^2/hr/F$)
HI = Inside heat transfer coefficient ($BTU/ft^2/hr/F$)
HNCON = Natural convection heat transfer from the hot gas ($BTU/ft^2/hr/F$)
HO = Outside heat transfer coefficient to the soil ($BTU/ft^2/hr/F$)
HRAD = Radiation heat transfer from the hot gas ($BTU/ft^2/hr/F$)
HYDD = Hydraulic diameter of building in direction of the hot gas flow (ft)
L = Length of building (ft)
PR = Prandtl number
QABS = Heat absorbed by the concrete (BTU)
QGAS = Heat released by the gas (BTU)
QHL1 = Heat loss to the soil (BTU)
QHL2 = Heat loss to air and heat loss to air infiltration (BTU)
QINF = Heat loss due to air infiltration (BTU)
QINS = Heat absorbed by the insulation (BTU)
QMET = Heat absorbed by the metal (BTU)
QTOTAL = Total heat loss (BTU)
RATIO = Dimensionless spacing interval
RE = Reynolds number
TAVG = Average Temperature of the hot gas (R)
TEMP1 = Current inside wall temperature (F)
TIME = Calculation time increment = 1 hr
TIN = Inlet gas temperature = 1500 or 2000 F
TO = Initial building temperature = 70 F
TOUT = Hot gas outlet temperature (F)
TW1= Inside wall temperature (F)
TW2 = Outside wall temperature (F)
VEL = Velocity of the hot gas (ft/sec)
VIS = Viscosity of the hot gas (lb/ft/sec)
W = Width of building (ft)
WINS = Weight of insulation = DINS X AREA2 X 10 lb/ft^3
WMET = Weight of metal = 10 ton X 2000 + other metal (lbs)

4.1.1.3 Step 2. The specific heat and average temperature of the hot gas is then calculated as follows:

$$TAVG = 460 + (TOUT + TIN)/2 = 1520\ R$$

$$CP^* = .2232 + 2.69\times10^{-5}\times TAVG = .2642\ BTU/lb/F$$

The heat released by the gas is calculated as follows:

$$QGAS = q_{gas} \times TIME = \dot{m} CP \Delta T$$

where $\dot{m}$ = FLOW(SCFM)x60(min./hr)x29(lb/lb-mole)/359(SCF/lb-mole)

TIME = 1 hr increment

CP = .2642 (BTU/lb/F)

ΔT = (TIN - TOUT)(F)

QGAS = 2000x60x29x1/359x.2642x(2000 - 70) = 4.9428×10^6 BTU

The effects of heat transfer by radiation, forced convection, natural convection, and conduction are considered in calculating the inside heat transfer coefficient as follows:

Radiation:

$$HRAD = \sigma \epsilon_{EFF}(TAVG^4\ T2^4)/(TAVG - T2)$$

where σ = 1.714×10^{-9} BTU/hr/ft^2/R^4

ϵ_{EFF} = Effective emissivity

T2 = TEMP1 + 460 = 70 + 460 = 530 R

TAVG = 1520 R

For combustion of methane in 100 percent excess air, the resulting flue gas contains 10 molar percent H_2O and 5 molar percent CO_2.

$$\text{Let } L = 3.4 \times \frac{\text{volume}}{\text{surface area}}$$

$$= 3.4 \left[\frac{H \times L \times W}{AREA1 + AREA2}\right]$$

$$= 3.4 \left[\frac{15 \times 150 \times 70}{17100 + 10500}\right] = 19.4$$

---

* Derived from physical properties of air at 30 to 2060 F.

$PwL = 0.1 \times 19.4 = 1.9$

At $TAVG = 1520\ R$, $\epsilon_w = 0.33$*

$PcL = 0.05 \times 19.4 = 1.0$

At $TAVG = 1520\ R$, $\epsilon_c = 0.15$**

The emissivity correction factor due to spectral overlap of water vapor and carbon oxide is neglected. The gas emissivity is then:

$$\epsilon_{GAS} = 0.33 + 0.15 = 0.48$$

$$\epsilon_{CONCRETE(unpainted)} = 0.63$$

$$\epsilon_{EFF} = \frac{1}{\frac{1}{0.48} + \frac{1}{0.63} - 1} = 0.37$$

$HRAD = 6.342 \times 10^{-10} \times (TAVG^4 - T2^4)/(TAVG - T2)$

$HRAD = 6.342 \times 10^{-10} \times (1520^4 - 530^4)/(1520 - 530) = 3.3690\ BTU/ft^2/hr/F$

Forced Convection:

$CONG^{***} = 4.077 \times 10^{-4} + 3.071 \times 10^{-5} \times TAVG - 6.557 \times 10^{-9} \times TAVG^2 + 7.890 \times 10^{-13} \times TAVG^3 = .0347\ BTU/ft/hr/F$

$VIS^{***} = (.2067 + 2.216 \times 10^{-3} \times TAVG - 5.779 \times 10^{-7} \times TAVG^2 + 8.031 \times 10^{-11} \times TAVG^3) \times 10^{-5} = 2.52 \times 10^{-5}\ lb/ft/sec$

$DENS^{***} = 39.733/TAVG = .0261\ lb/ft^3$

$VEL = FLOW(SCFM) \times TAVG(F)/CSAREA(ft^2)/60(sec/min)/492(F)$

$VEL = 2000 \times 1520 \times /1050/60/492 = .098\ ft/sec$

---

* Table 4-15 from Heat Transmission by W. H. McAdams, pub. by McGraw-Hill, 1954.

** IBID, Table 4-13.

*** Derived from physical properties of air at 30 to 2060 F.

$RE = HYDD(ft) x DENS(lb/ft^3) x VEL(ft/sec)/VIS(lb/ft/sec)$

$RE = 24.7 x .0261 x .098/2.52 x 10^{-5} = 2507$

$PR = VIS(lb/ft/sec) x CP(BTU/lb/F) x 3600(sec/hr)/CONG(BTU/ft/hr/F)$

$PR = 2.52 x 10^{-5} x .2642 x 3600/.0347 = .6907$

HFCON = Nu x CONG/HYDD

where CONG = .0347 BTU/ft/hr/F

HYDD = 24.7 ft

$Nu = .023\ RE^{.8} PR^{.3}$**

RE = 2507

PR = .6907

$HFCON = (CONG/HYDD) x .023 x RE^{.8} x PR^{.3}$

$HFCON = .0347/24.7 x .023 x 2507^{.8} x .6907^{.3} = .01515$
$BTU/ft^2/hr/F$

Natural Convection:

$BETA^* = (4.17 - 6.088 x 10^{-3} x TAVG + 3.684 x 10^{-6} x TAVG^2 -$

$7.312 x 10^{-10} x TAVG^3) x 10^{-3} = .684 x 10^{-3}\ F^{-1}$

$GR = DENS^2(lb^2/ft^6) x 32.174(ft/sec^2) x BETA(F^{-1}) x HYDD^3(ft^3) x$
$(TAVG - T2)(F)/VIS^2(lb^2/ft^2/sec^2)$

$GR = (.0261)^2 x 32.174 x .000684 x (24.7)^3 x (1520 - 530)/(2.52 x 10^{-5})^2$

$GR = 3.5213 x 10^{11}$

---

* Derived from physical properties of air at 30 to 2060 F.

** For a fluid being cooled under turbulent conditions. See p. 365 of Fundamentals of Momentum, Heat and Mass Transfer, 2nd ed., by J. R. Welty et al., publ. by John Wiley & Sons, 1976.

HNCON = Nu x CONG/HYDD

where CONG = .0347 BTU/ft/hr/F

HYDD = 24.7 ft

Nu = $.548(GRPR)^{.25}$*

GR = $3.5218\text{x}10^{11}$

PR = .6907

HNCON = $(CONG/HYDD)x.548x(GRxPR)^{.25}$

HNCON = $.0347/24.7x.548x(3.5218x10^{11}x.6907)^{.25}$

= .5407 BTU/ft^2/hr/F

Conduction:

HCOND = CONG/$\sqrt{(4\ \alpha_{gas}\ x\ TIME)}$

where CONG = .0347 BTU/ft/hr/F

TIME = 1 hr

α_{gas} = CONG/(DENSxCP)

CP = .2642 BTU/lb/F

HCOND = .0347/$\sqrt{(4x1x.0347/(.0261x.2642))}$ = .0077 BTU/ft^2/hr/F

The total inside heat transfer coefficient is:

HI = HRAD + HFCON + HNCON + HCOND

HI = 3.3690 + .01515 + .5407 + .0077 = 3.9325 BTU/ft^2/hr/F

4.1.1.4 Step 3:

The inside wall temperature is calculated as follows:

TW1 = TOUT - QGAS/(TIMExHIx(AREA1 + AREA2))

TW1 = 120 - $4.9428\text{x}10^6$/(1x3.9325x(17100 + 10500))

= 75.649 F

* For a vertical surface. I.12 pg. 354.

4.1.1.5 Step 4:

The temperature profile in concrete is calculated as follows:

DELX = DEPTH/INVL = 1/12 = .0833 ft

$RATIO = TIME \times ALPHA/DELX^2$

$RATIO = 1 \times .023/.0833^2$

$HO = CSOIL/\sqrt{(4 \times \alpha_{SOIL} \times TIME)}$

where CSOIL = .3 BTU/ft/hr/F

TIME = 1 hr

α_{soil} = CSOIL/(CPSOILxDENSSL)

CPSOIL = .44 BTU/lb/F

DENSSL = 128 lb/ft^3

$HO = .3/\sqrt{(4 \times 1 \times .3/(.44 \times 128))} = 2.0552$ BTU/ft^2/hr/F

BIOT = Biot number = HO x L/CCON

where HO = 2.0552 BTU/ft^2/hr/F

DEPTH = 1 ft

CCON = .7 BTU/ft/hr/F

BIOT = 2.0552x1/.7 = 2.936

These values are then used to calculate the temperature profile. The temperature profile was calculated using an implicit differential method.* The recursion formula was:

$$-RATIO \times T_{i-1,j+1} + (1 + 2 \times RATIO) \times T_{i,j+1} - RATIO \times T_{i+1,j+1} = T_{i,j}$$

where T = temperature

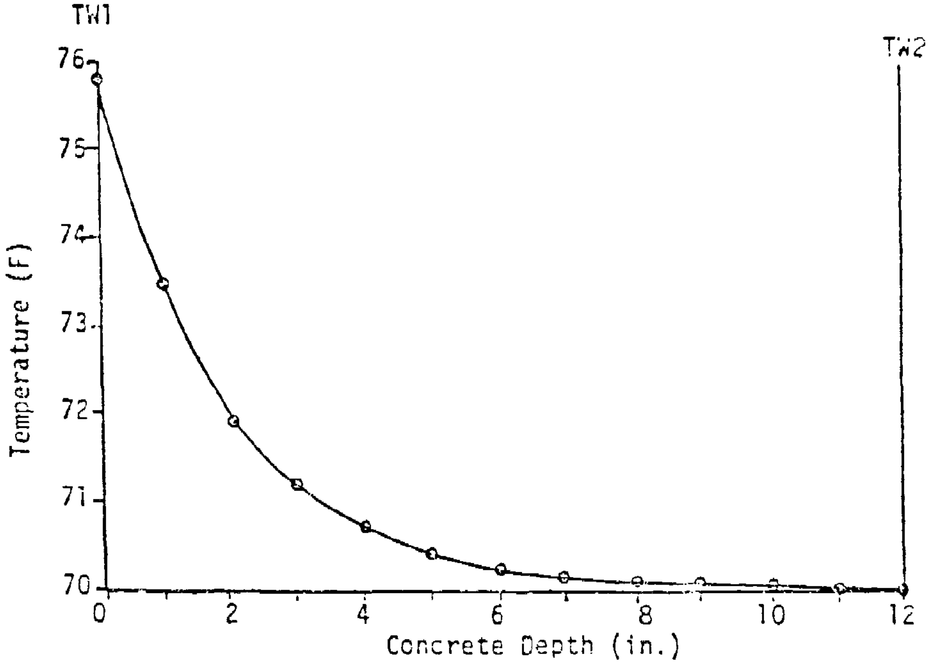
i = depth increment

j = time increment

---

* Applied Numerical Methods by B. Carnahan, et al., 1969.

For the first iteration the following profile is generated:



For the heat absorbed by metal in the building:

$$QMET = CPMET \times WMET \times (TW2_{CURRENT} - TW2_{PREVIOUS})/2 \times TIME$$

where

$$WMET = 10 \times 2000 + \frac{0.05^*}{12} \times AREA2 \times 488 = 41350 \text{ lb}$$

$$QMET = 0.11 \times 41350 \times (70.01 - 70)/2 \times 1 = 23$$

For the first iteration the average temperature increase of the concrete wall is calculated as follows:

---

* 18 gauge sheet metal is used to enclose the basement of Building 1.

$$TA = \frac{1}{12}\sum_{I=1}^{12}(T_{ave}(I+1) - T_{ave}(I))$$

$$TA = \frac{1}{12}((75.65 + 73.29)/2 - (70 + 70)/2) + ((73.29 - 71.91)/2 - (70 + 70)/2) + \ldots\ldots + ((70.02 - 70.01)/2 - (70 + 70)/2)$$

$$TA = .89\ F$$

4.1.1.6 Step 5. The heat balances yield the following results:

For the heat absorbed by the concrete wall:

$Q_{ABS} = q_{abs} \times TIME = CMASS \times CPCON \times TA \times TIME$

where TA = .89 F

CPCON = .21 BTU/lb/F

CMASS = AREA1xDEPTHxDENSC

AREA1 = 17100 ft^2

DEPTH = 1 ft

DENSC = 144 lb/ft^3

TIME = 1 hr

$QABS = 17100 \times 1 \times 144 \times .21 \times .89 = 4.6022 \times 10^5$ BTU

For the heat absorbed by the insulation on the building exterior:

$QINS = CPINS \times WINS^* (TW2_{CURRENT} - TW2_{PREVIOUS})/2 \times TIME$

$= 0.2 \times 0.1667^* \times (70.01 - 70.0) \times 1$

QINS = 0

For the heat loss to the soil:

$QHL1 = q_{hl} \times TIME = HO \times AREA1\ (TW2 - TO) \times TIME$

where AREA1 = 17100 ft^2

TIME = 1 hr

TW2 = 70.012 F

TO = 70 F

HO = 2.0552 $BTU/ft^2/hr/F$

$QHL1 = 2.0552 \times 17100 \times (70.012 - 70) = 422$ BTU

For the heat loss due to air infiltration into the building through cracks and other small openings:

---

* For 2 inches of insulation.

$$QINF = q_{inf}xTIME = \dot{m}Cp(TW1 - TO) \times TIME$$

where $Cp = .24$ BTU/lb/F

$TW1 = 75.649$ F

$TO = 70$ F

$\dot{m}$ = FINF(SCFM)x60(min/hr)x29(lb/lb-mole)/359(SCF/lb-mole)

FINF = 100 SCFM

TIME = 1 hr

QINF = 100x60x1x29/359x.24x(75.649 - 70) = 657 BTU

For the heat loss to the air:

$$QHL2 = q_{hl}xTIME = U \times AREA2 \times (TW1 - TO) \times TIME$$

where AREA2 = 10500 ft^2

TW1 = 75.649 F

TO = 70 F

U = 1/(DINS/CINS + 1/4.6)

DINS = .3333 ft

CINS = .05 BTU/ft/hr/F

TIME = 1 hr

QHL2 = 1/(.3333/.05 + 1/4.6)x10500x1x(75.649 - 70) = 3617 BTU

The total heat absorbed/lost is:

QTOTAL = QABS + QINS + QMET + QHL1 + QHL2 + QINF

QTOTAL = 460,220 + 0 + 23 + 422 + 8617 + 657 = 469,939 BTU

4.1.1.7 Step 6. Next, QABS and QTOTAL are compared and TOUT is incremented until QABS and QTOTAL converge (i.e., repeat steps 1-5).

4.1.1.8 Example Output. An example computer output is given in Figure 4. Heating curves for the application of 2000 scfm of 2000 F hot gas to Building 1 are illustrated in Figure 5.

```
BUILDING HEAT TRANSFER CALCULATIONS:TASK 3-BLDG. #3

FLOW=2000.00 SCFM.  TIN= 2000.00 DEGREES F.  DINS=   .1667 FEET.

ITERATION NUMBER   5  TIME= 5.00 HOURS

THE TEMPERATURE PROFILE AT TIME  5.00 IS:
 397.44 332.50 277.30 230.89 193.01
 162.81 139.23 121.20 107.73  97.94
  91.10  86.66  84.22
TOUT= 438.99  HI= 6.0888  TW1= 397.44  TW2=  84.22  HO=  .9191
QABS=.283E+07 QHL1=.653E+05 QHL2=.105E+07 QINF=.381E+05 QINS=.325E+05
QMET=.666E+05 QGAS=.406E+07 QTOTAL=.407E+07

ITERATION NUMBER  10  TIME=10.00 HOURS

THE TEMPERATURE PROFILE AT TIME 10.00 IS:
 489.48 433.19 381.62 335.07 293.66
 257.41 226.20 199.83 178.05 160.56
 147.05 137.26 130.92
TOUT= 523.94  HI= 6.9634  TW1= 489.48  TW2= 130.92  HO=  .6499
QABS=.226E+07 QHL1=.198E+06 QHL2=.135E+07 QINF=.488E+05 QINS=.262E+05
QMET=.333E+05 QGAS=.386E+07 QTOTAL=.386E+07

ITERATION NUMBER  15  TIME=15.00 HOURS

THE TEMPERATURE PROFILE AT TIME 15.00 IS:
 545.42 495.31 448.44 405.08 365.41
 329.60 297.72 269.79 245.80 225.68
 209.35 196.69 187.56
TOUT= 576.22  HI= 7.5299  TW1= 545.42  TW2= 187.56  HO=  .5377
QABS=.185E+07 QHL1=.312E+06 QHL2=.153E+07 QINF=.553E+05 QINS=.177E+05
QMET=.225E+05 QGAS=.373E+07 QTOTAL=.373E+07

ITERATION NUMBER  20  TIME=20.00 HOURS

THE TEMPERATURE PROFILE AT TIME 20.00 IS:
 586.64 541.37 498.61 458.60 421.52
 387.53 356.76 329.27 305.12 284.32
 266.35 252.68 241.72
TOUT= 615.02  HI= 7.9634  TW1= 586.64  TW2= 241.72  HO=  .4596
QABS=.155E+07 QHL1=.395E+06 QHL2=.166E+07 QINF=.601E+05 QINS=.139E+05
QMET=.176E+05 QGAS=.364E+07 QTOTAL=.364E+07

ITERATION NUMBER  25  TIME=25.00 HOURS

THE TEMPERATURE PROFILE AT TIME 25.00 IS:
 619.58 578.32 539.10 502.14 467.60
 435.62 406.34 379.84 356.18 335.40
 317.52 302.51 290.34
TOUT= 646.15  HI= 8.3238  TW1= 619.58  TW2= 290.34  HO=  .4110
QABS=.132E+07 QHL1=.453E+06 QHL2=.177E+07 QINF=.639E+05 QINS=.112E+05
QMET=.142E+05 QGAS=.356E+07 QTOTAL=.356E+07

ITERATION NUMBER  27  TIME=27.00 HOURS

THE TEMPERATURE PROFILE AT TIME 27.00 IS:
 631.10 594.26 553.32 517.47 483.80
 452.69 424.01 397.94 374.55 353.87
 335.92 320.69 308.16
TOUT= 657.07  HI= 8.4529  TW1= 631.10  TW2= 308.16  HO=  .3955
QABS=.124E+07 QHL1=.471E+06 QHL2=.180E+07 QINF=.657E+05 QINS=.103E+05
QMET=.130E+05 QGAS=.357E+07 QTOTAL=.354E+07
```

FIGURE 4. EXAMPLE COMPUTER OUTPUT FOR THE HOT GAS DECONTAMINATION HEAT BALANCE CALCULATIONS

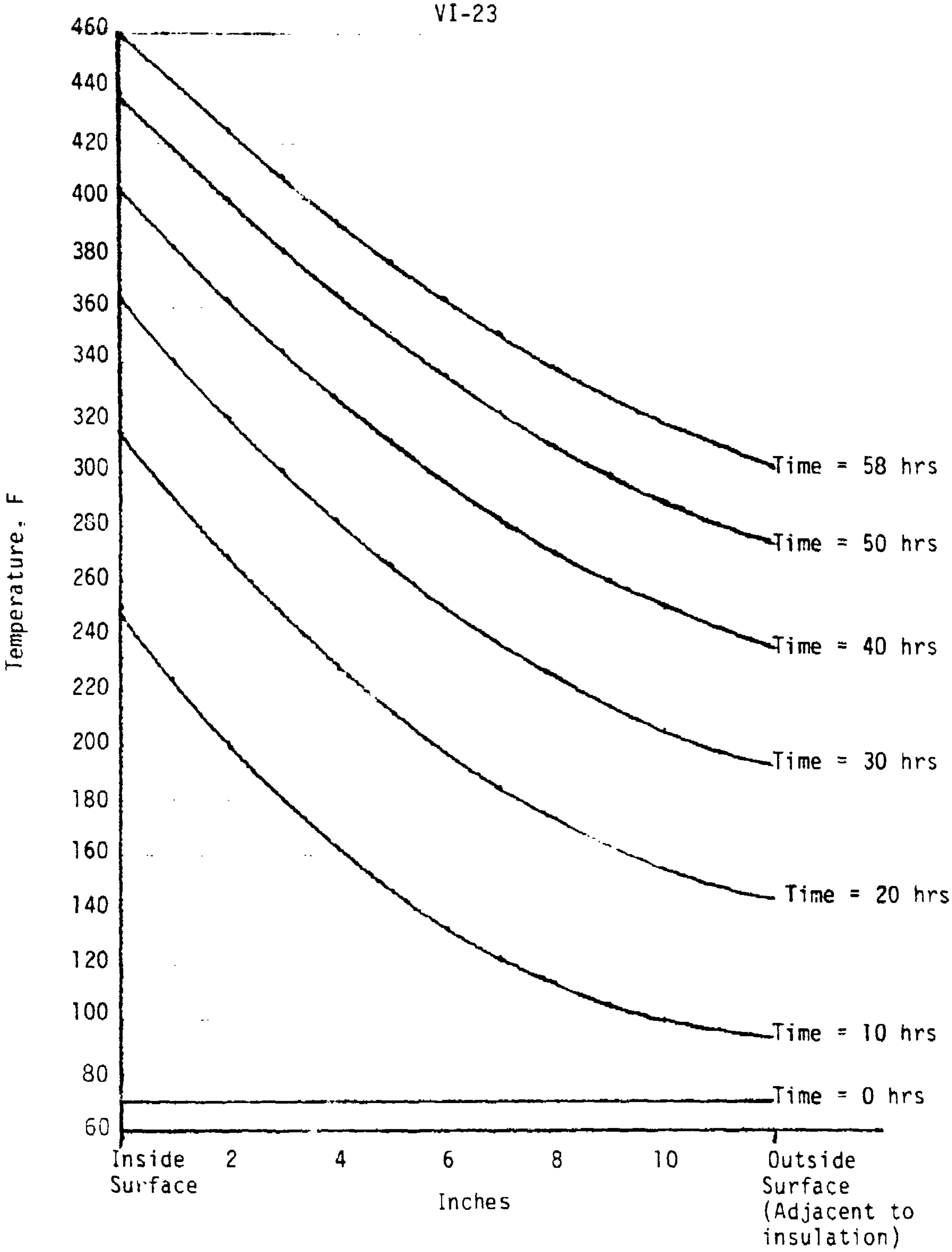


FIGURE 5. TEMPERATURE PROFILES IN THE CONCRETE WALLS OF BUILDING 1 DURING APPLICATION OF THE HOT GAS DECONTAMINATION PROCESS (2000 scfm/2000 F)

4.1.2 Results of Hot Gas Heat Transfer Calculations

The results of the heat transfer calculations for the three buildings are given in Tables 3 through 5.

Heating time versus hot gas flow rate curves for varying hot gas inlet temperatures and insulation thicknesses are illustrated in Figure 6 (Building 1), Figure 7 (Building 2) and Figure 8 (Building 3).

Fuel requirement versus hot gas flow rate curves for varying hot gas inlet temperatures and insulation thicknesses are illustrated in Figure 9 (Building 1), Figure 10 (Building 2) and Figure 11 (Building 3).

Final inside wall temperature versus hot gas flow rate curves for varying hot gas inlet temperatures and insulation thicknesses are illustrated in Figure 12 (Building 1), Figure 13 (Building 2) and Figure 14 (Building 3).

It is interesting to note that for Building 2, an increase in insulation thickness results in a decrease in the final inside wall temperature (see Figure 13). This is opposite to the trends observed for Buildings 1 and 3 (see Figures 12 and 14, respectively). In general, as the insulation thickness increases, the heat losses from the building decrease. This causes a decrease in the heat-up time which should, in turn, result in a lower wall temperature. Factors which would affect these trends include the following:

- Type of surfaces being insulated. In Building 2, the insulation was placed on concrete walls whereas in Buildings 1 and 3 the insulation was placed on metal surfaces. Also, all of the concrete from Buildings 1 and 3 is uninsulated and exposed to the surrounding soil which serves as a heat sink/insulator.
- Area of surfaces being insulated. The total insulated area was 10,500 ft^2 for Building 1, 4,800 ft^2 per floor for Building 2, and 11,000 ft^2 for Building 3.

TABLE 3. RESULTS OF HEAT BALANCES FOR HOT GAS DECONTAMINATION OF BUILDING 1[a]

Hot Gas Flow Rate, SCFM	Inlet Gas Temperature, F	Insulation Thickness,[b] Inches	Time to Reach Temperature,[c] Hours	Burner Heat Duty, MM BTU/hr	CH_4 Required,[d] 1000 SCF	Wall Temperature at End[e] F
1000	1500	2	291	2.43	720	345
		4	186		460	365
		12	152		376	378
	2000	2	138	3.07	444	377
		4	111		357	397
		12	98		315	410
2000	1500	2	91	4.37	398	408
		4	78		341	427
		12	72		315	440
	2000	2	58	5.66	328	462
		4	53		300	484
		12	50		283	498
3000	1500	2	58	6.32	365	459
		4	53		335	481
		12	50		316	493
	2000	2	40	8.25	330	537
		4	37		305	557
		12	36		297	573
4000	1500	2	44	8.26	363	503
		4	41		339	524
		12	40		330	542
	2000	2	31	10.84	336	597
		4	30		325	624
		12	29		314	638

(a) Building 1 is modeled after Building 412 of Rocky Mt. Arsenal. It is 150 feet long by 70 feet wide by 15 feet high concrete (one foot thick) basement with wood superstructure. It is assumed the wood structure is removed and incinerated leaving a concrete-lined basement requiring decontamination.
(b) Girders and steel plates are placed over the basement to contain the hot gas. Insulation is then placed on the steel plates to reduce heat losses.
(c) Time required for the outside wall temperature to reach 300 F.
(d) Natural gas was assumed to be the fuel source.
(e) Inside wall temperature at end of heat-up.

TABLE 4. RESULTS OF HEAT BALANCES FOR HOT GAS DECONTAMINATION OF BUILDING 2[(a)]

Hot Gas Flow Rate, SCFM	Inlet Gas Temperature, F	Insulation Thickness,[(b)] Inches	Time to Reach Temperature,[(c)] Hours	Burner Heat Duty, MM BTU/hr	CH_4 Required,[(d)] 1000 SCF	Wall Temperature at End[(e)] F
1000	1500	2	252	2.43	612	742
		4	169		411	626
		12	133		323	552
	2000	2	161	3.07	494	825
		4	122		375	716
		12	103		316	650
2000	1500	2	130	4.37	568	859
		4	105		459	758
		12	87		380	706
	2000	2	95	5.66	538	1009
		4	79		447	923
		12	70		396	866
3000	1500	2	100	6.32	632	944
		4	81		512	868
		12	71		449	818
	2000	2	74	8.25	611	1146
		4	64		528	1075
		12	58		479	1026
4000	1500	2	85	8.26	702	1015
		4	71		586	952
		12	63		520	907
	2000	2	64	10.84	694	1255
		4	56		607	1191
		12	51		553	1144

(a) Building 2 is modeled after Building 1501 of Rocky Mt. Arsenal. It has three stories, each 80 feet long by 40 feet wide by 20 feet high. The walls are 2-ft thick reinforced concrete and the floors and ceiling are 1-ft thick concrete.
(b) Insulation is used to reduce heat losses through the concrete walls/ceiling.
(c) Time required for the outside wall temperature of the concrete on the first floor to reach 300 F.
(d) Natural gas was assumed to be the fuel source.
(e) *Inside wall temperature at end of heat-up.*

TABLE 5. RESULTS OF HEAT BALANCES FOR HOT GAS DECONTAMINATION OF BUILDING 3[a]

Hot Gas Flow Rate, SCFM	Inlet Gas Temperature, F	Insulation Thickness,[b] Inches	Time to Reach Temperature,[c] Hours	Burner Heat Duty, MM BTU/hr	CH_4 Required,[d] 1000 SCF	Wall Temperature at End[e] F
1000	1500	2	97	2.43	240	388
		4	61		151	442
		12	41		132	522
	2000	2	52	3.07	167	458
		4	51		126	487
		12	36		116	566
2000	1500	2	38	4.37	166	509
		4	32		140	572
		12	30		131	620
	2000	2	27	5.66	153	631
		4	24		136	706
		12	23		130	759
3000	1500	2	27	6.32	171	604
		4	25		158	676
		12	24		152	726
	2000	2	20	8.25	165	762
		4	19		157	849
		12	18		149	895
4000	1500	2	23	8.26	190	685
		4	21		173	754
		12	20		165	799
	2000	2	17	10.84	184	872
		4	16		173	956
		12	16		173	1014

(a) Building 3 is modeled after Building 1640 of Rocky Mt. Arsenal. It is 100 feet long by 50 feet wide by 20 feet high metal wall/ceiling structure with a one-foot thick concrete floor.
(b) Insulation is used to reduce heat losses through the metal walls/ceiling.
(c) Time required for the outside wall temperature of the concrete to reach 300 F.
(d) Natural gas was assumed to be the fuel source.
(e) Inside wall temperature at end of heat-up.

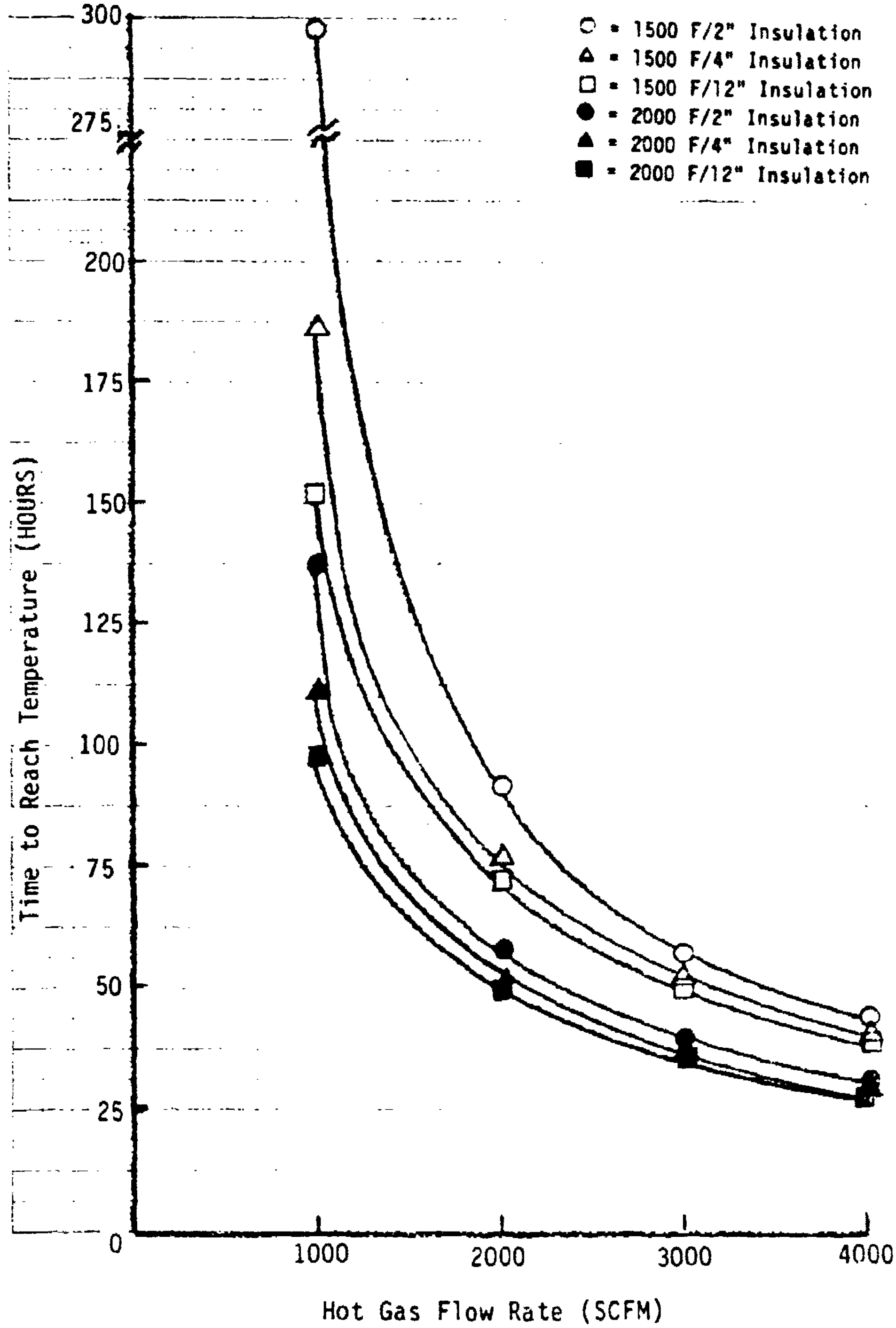


FIGURE 6. HEATING TIMES VERSUS HOT GAS FLOW RATES FOR BUILDING 1

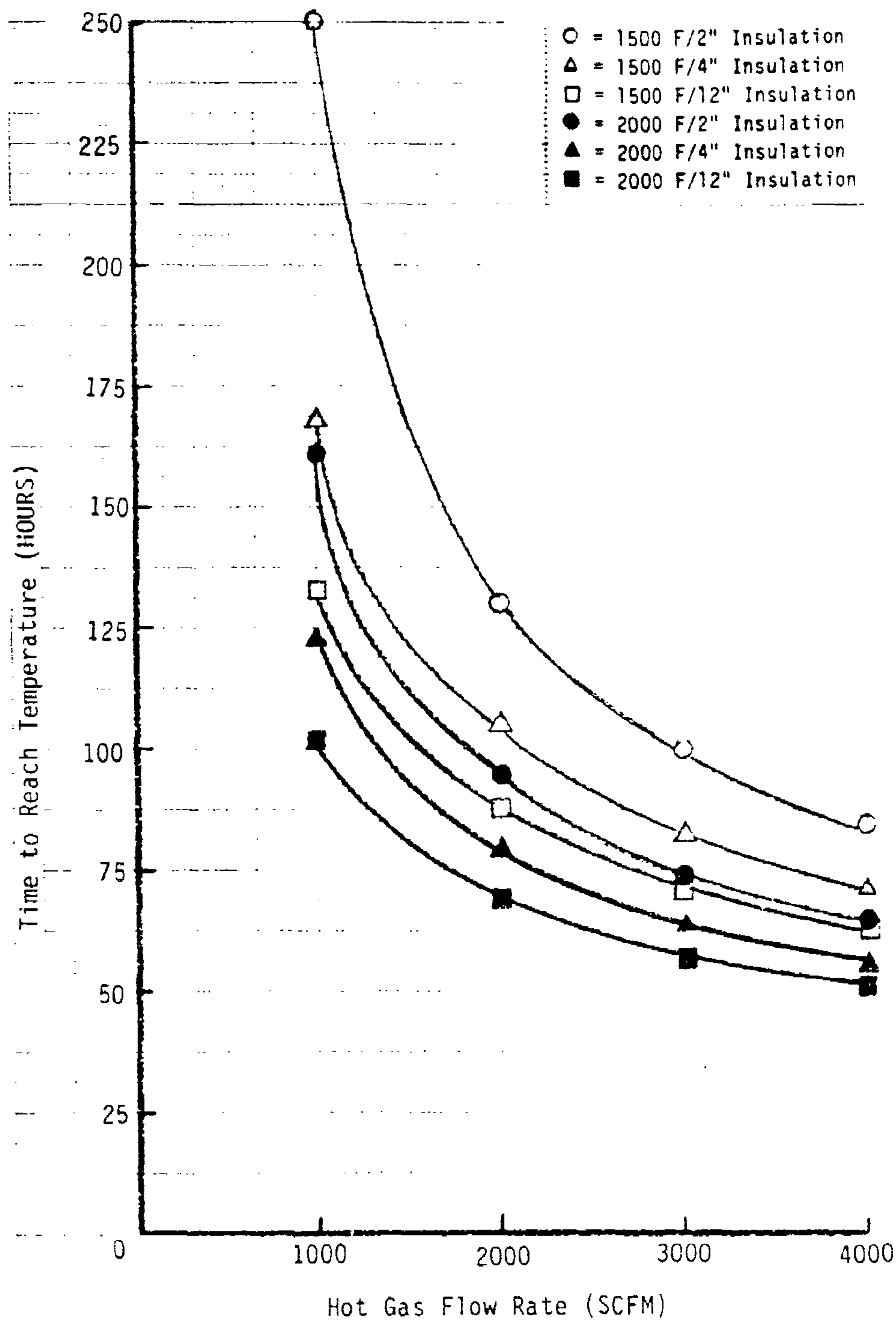


FIGURE 7. HEATING TIMES VERSUS HOT GAS FLOW RATES FOR BUILDING 2

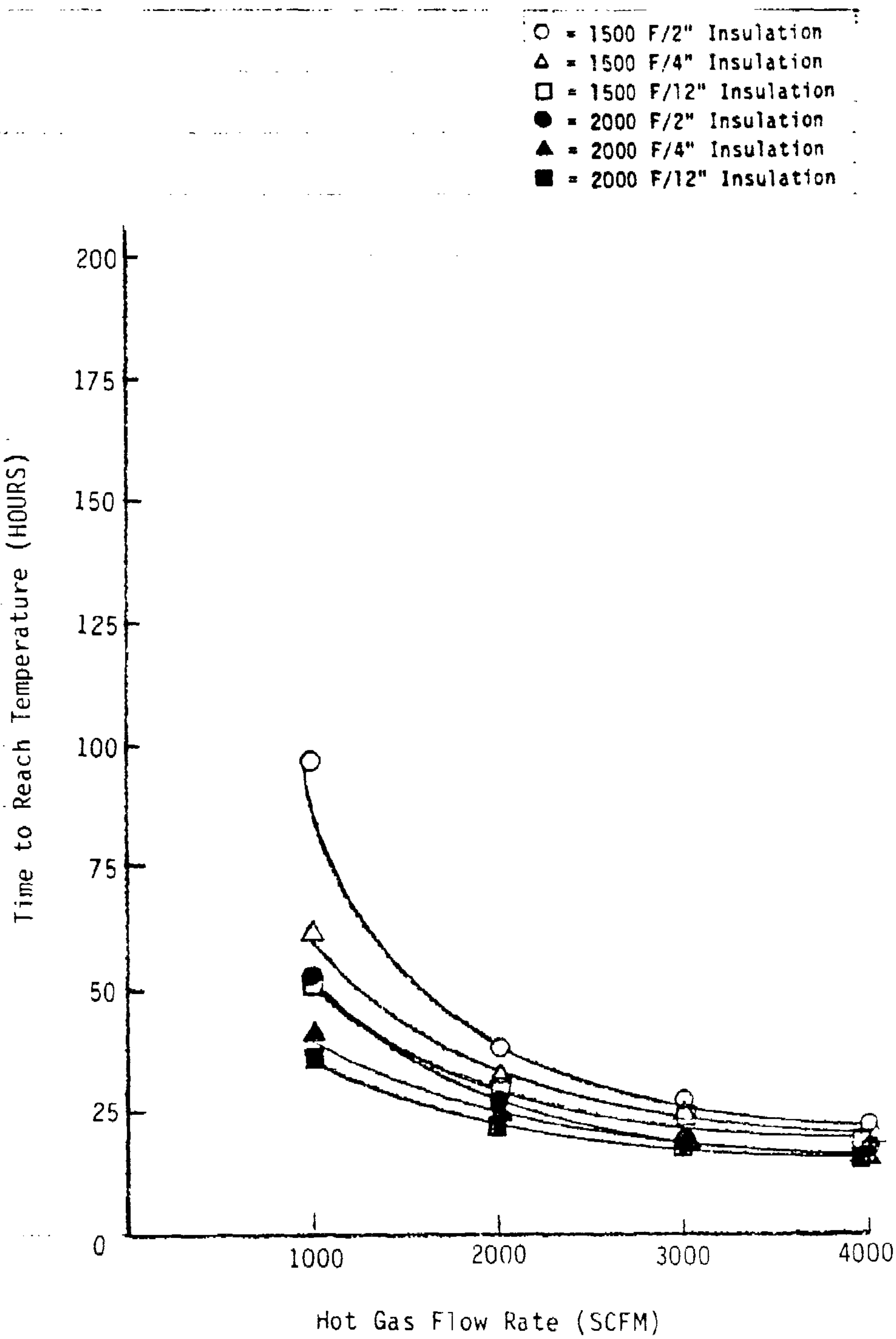


FIGURE 8. HEATING TIMES VERSUS HOT GAS FLOW RATES FOR BUILDING 3

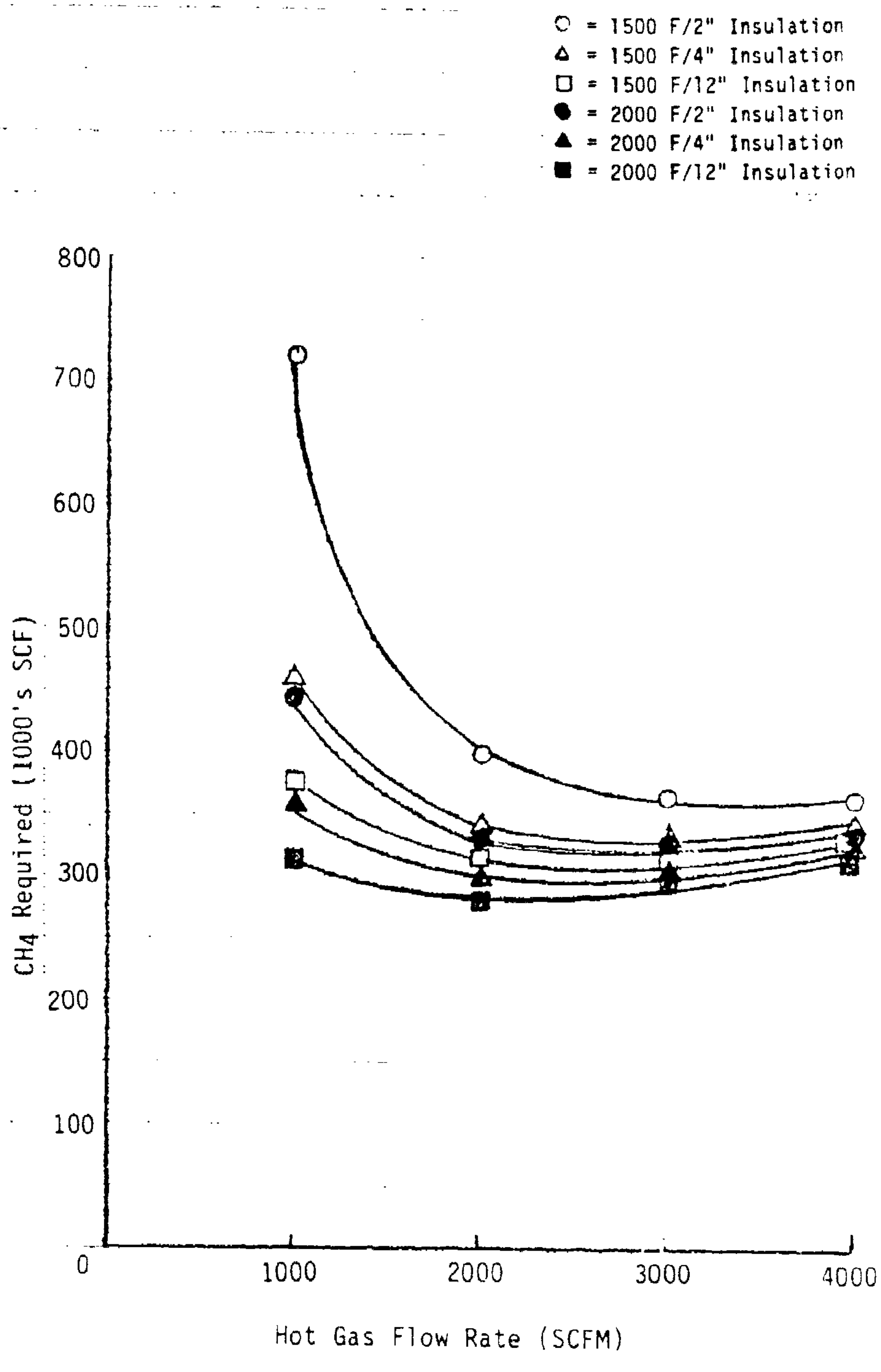


FIGURE 9. FUEL REQUIREMENTS VERSUS HOT GAS FLOW RATES FOR BUILDING 1

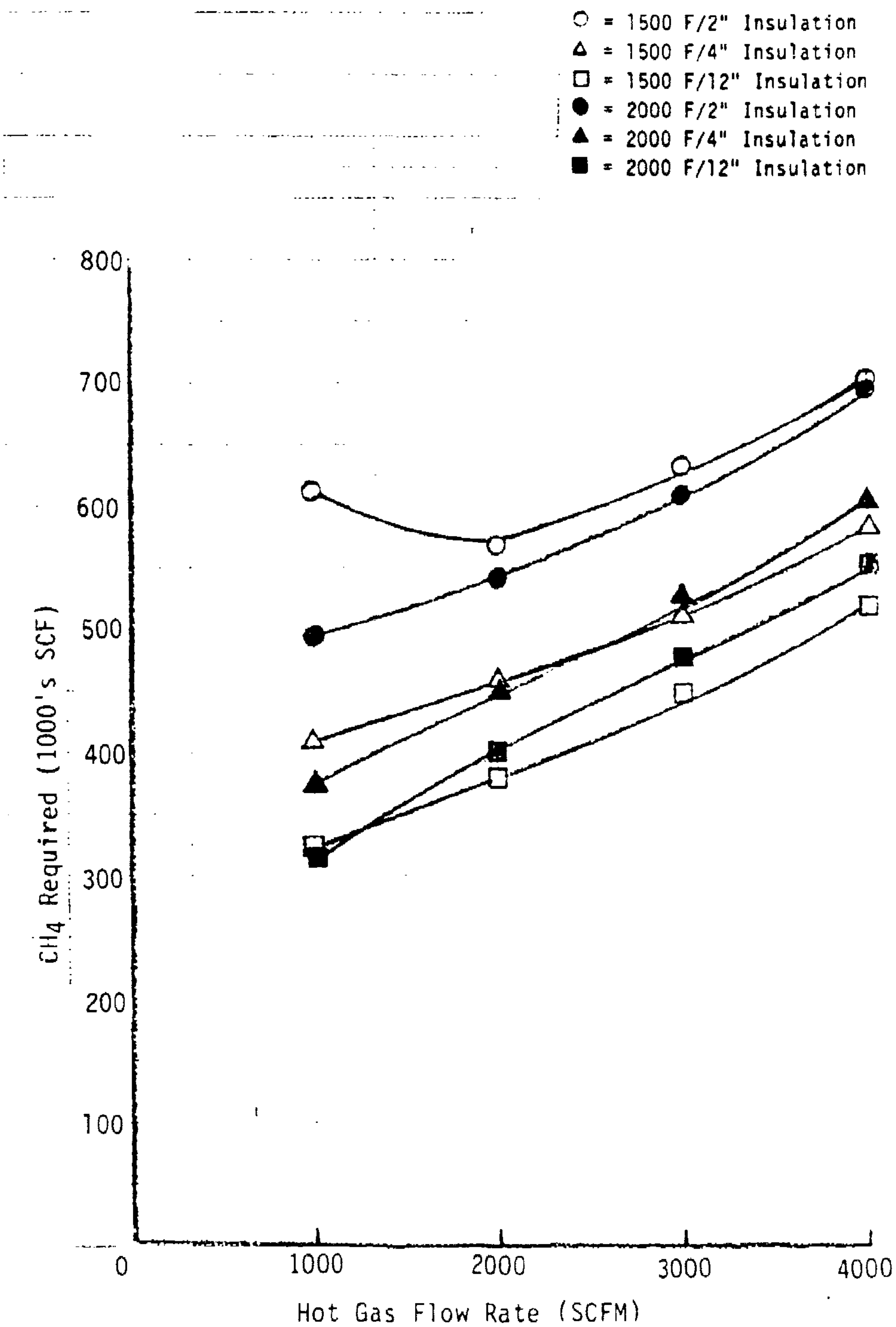


FIGURE 10. FUEL REQUIREMENTS VERSUS HOT GAS FLOW RATES FOR BUILDING 2

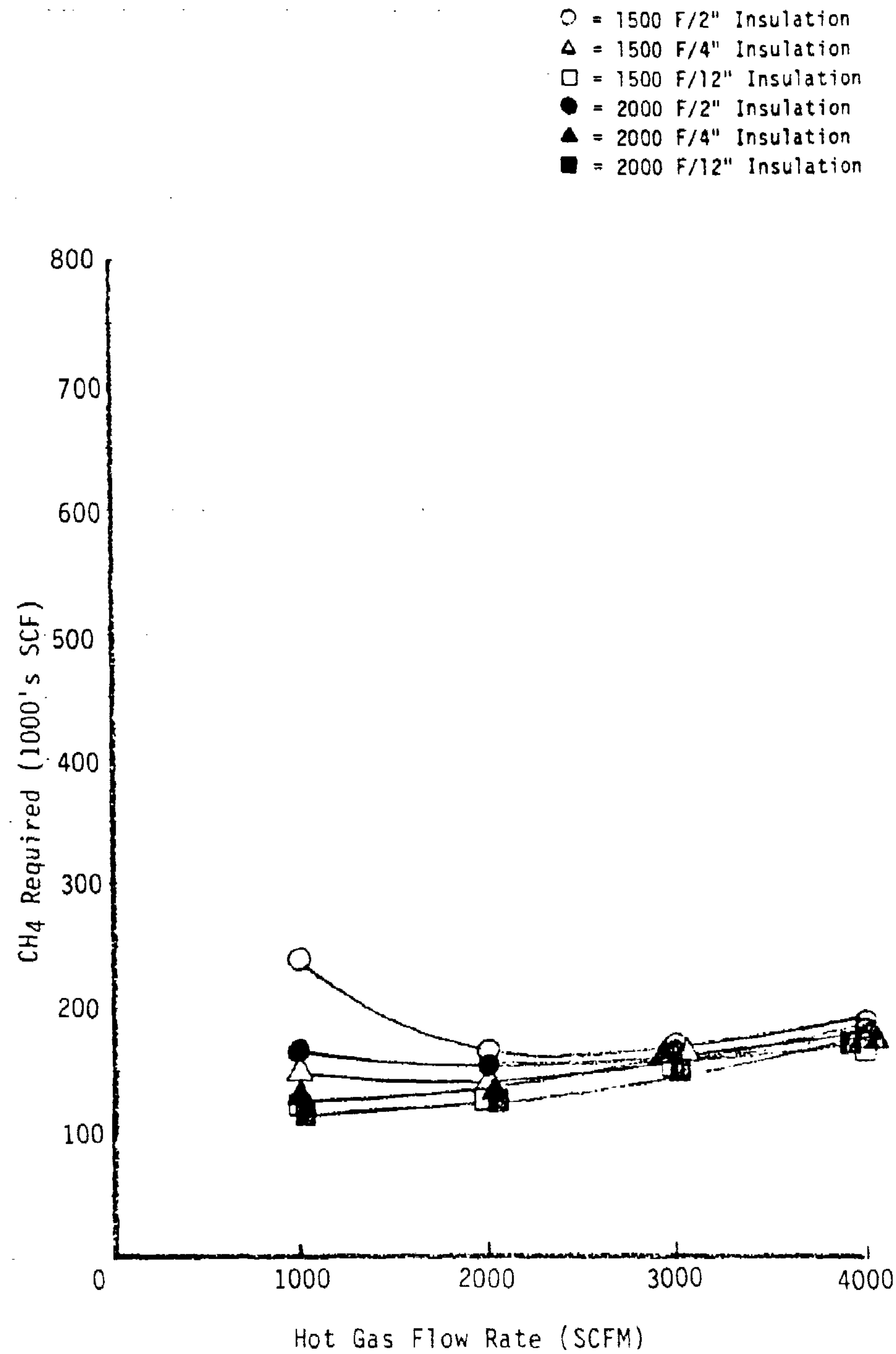


FIGURE 11. FUEL REQUIREMENTS VERSUS HOT GAS FLOW RATES FOR BUILDING 3

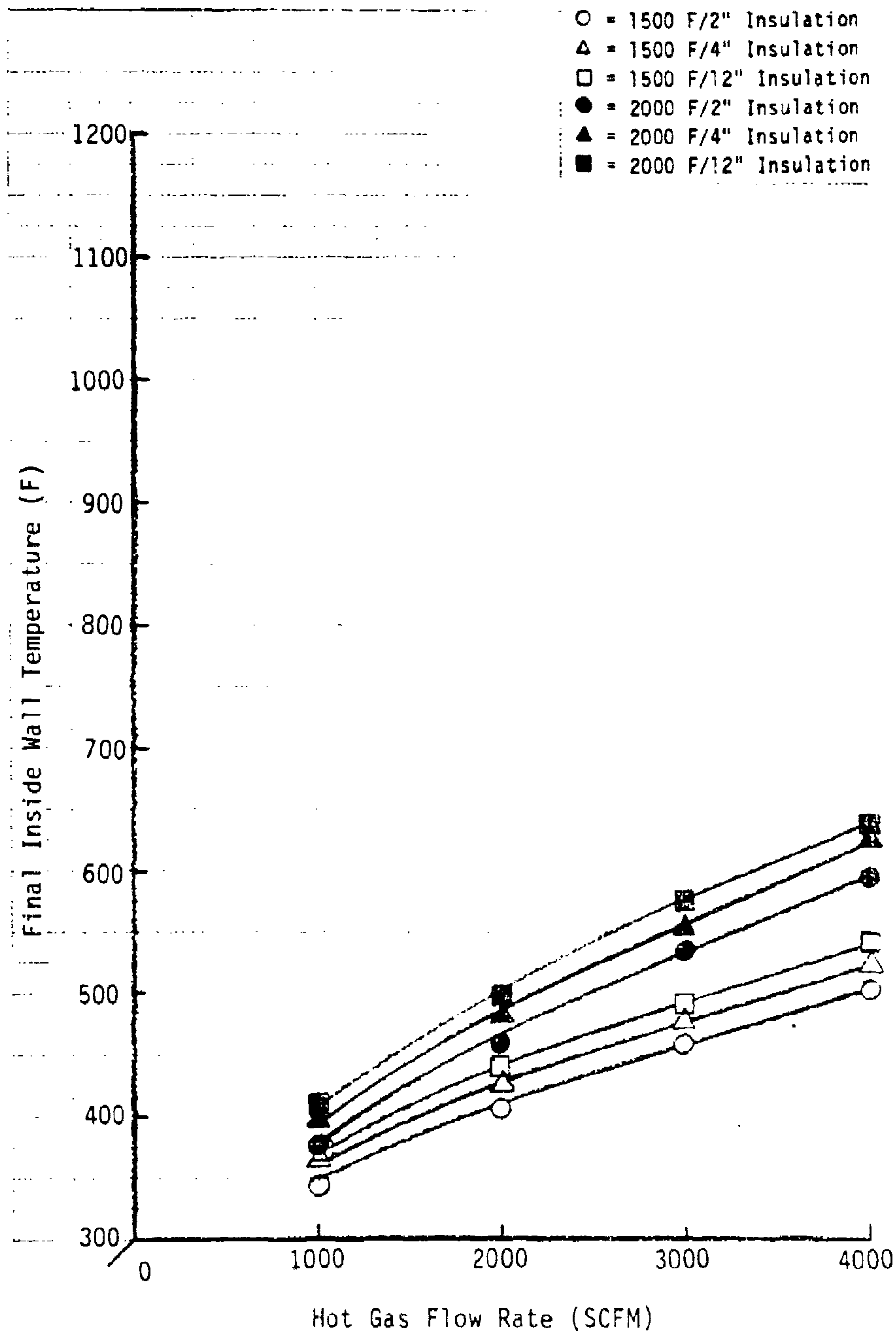


FIGURE 12. FINAL INSIDE WALL TEMPERATURE VERSUS HOT GAS FLOW RATES FOR BUILDING 1

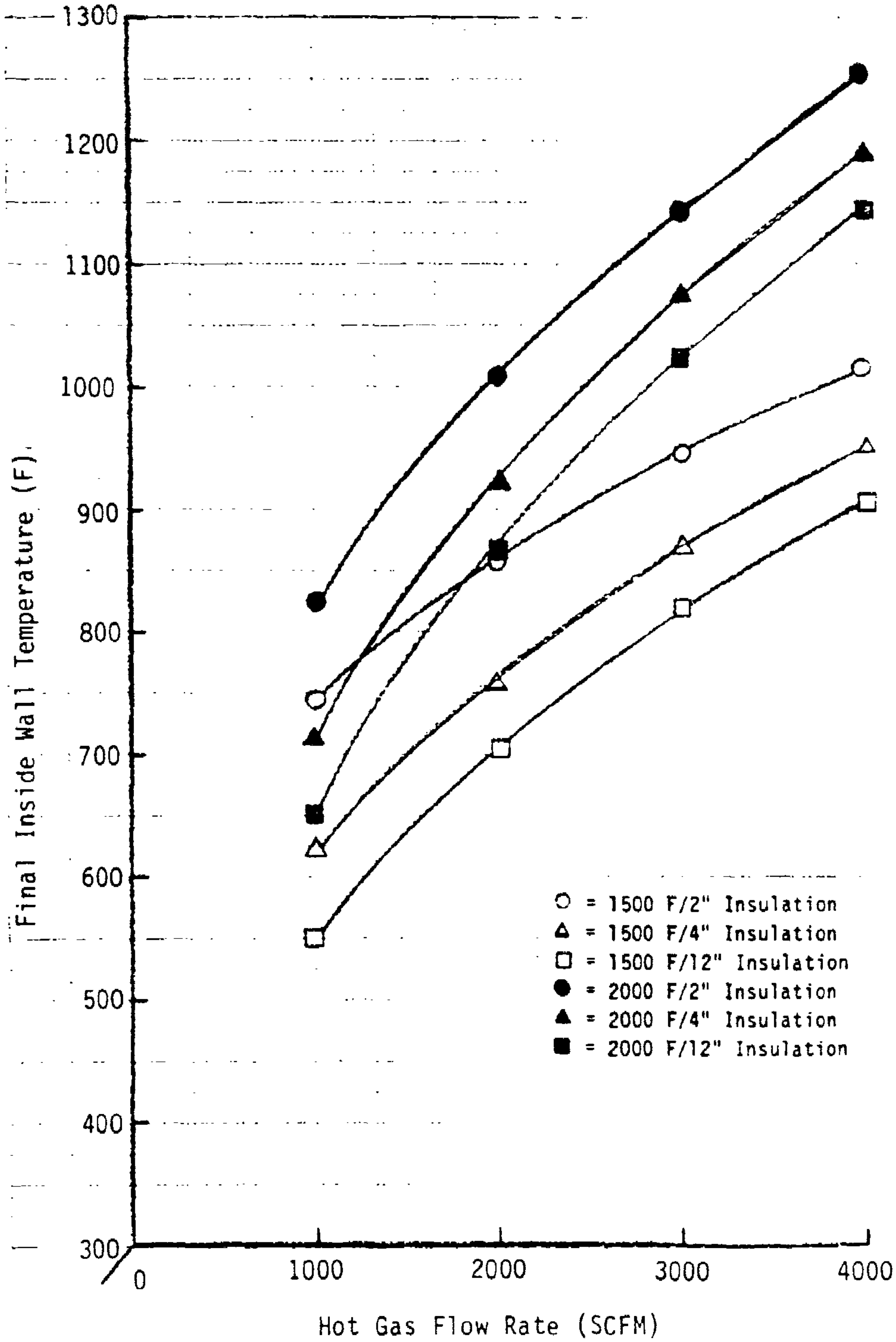


FIGURE 13. FINAL INSIDE WALL TEMPERATURE VERSUS HOT GAS FLOW RATES FOR BUILDING 2

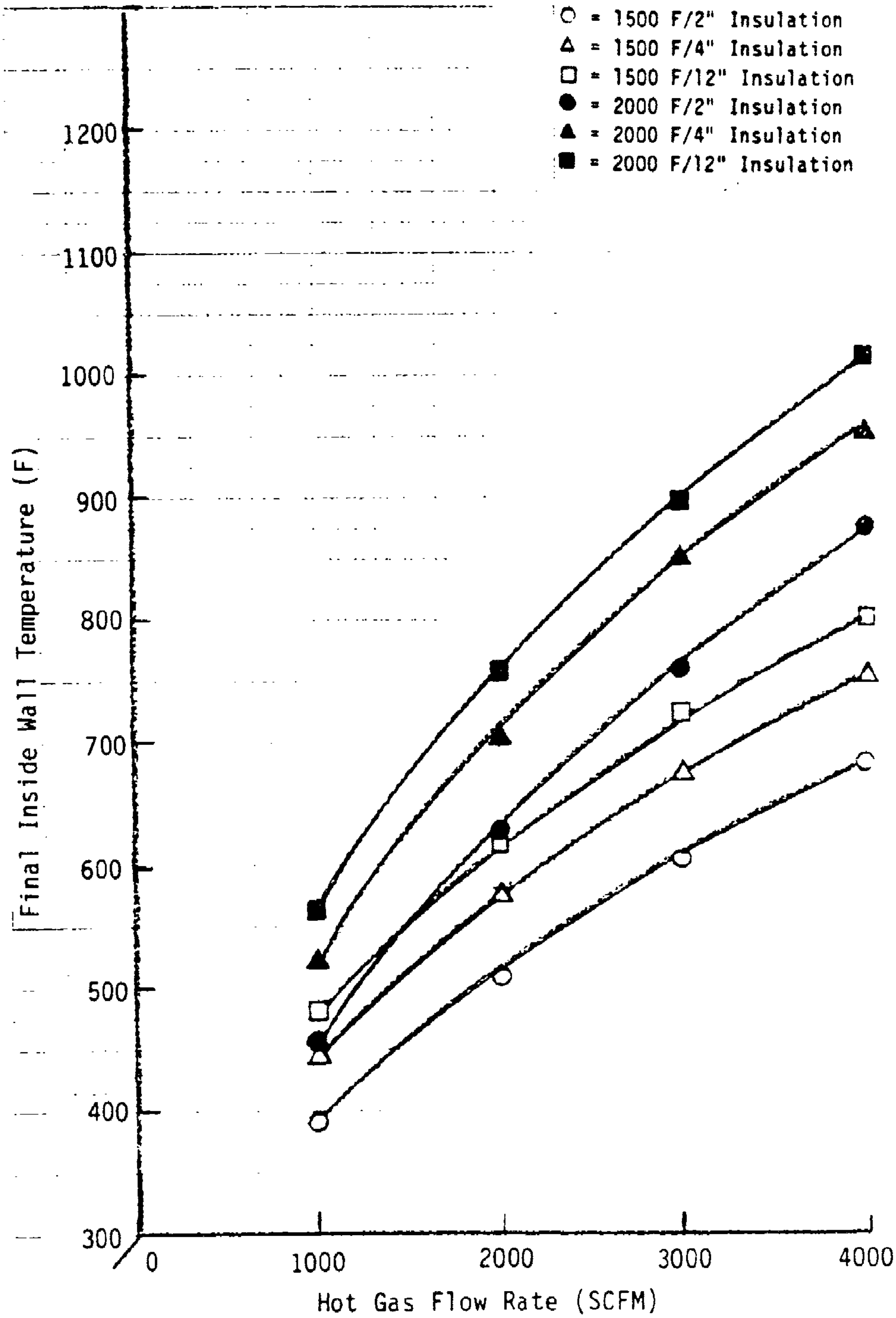


FIGURE 14. FINAL INSIDE WALL TEMPERATURE VERSUS HOT GAS FLOW RATES FOR BUILDING 3

- Thickness of building material. The material thickness (i.e. mass) will determine the response to heating and the subsequent temperature profile and thermal inertia in the material.

4.2 Hot Gas Decontamination Equipment Selection/Costing

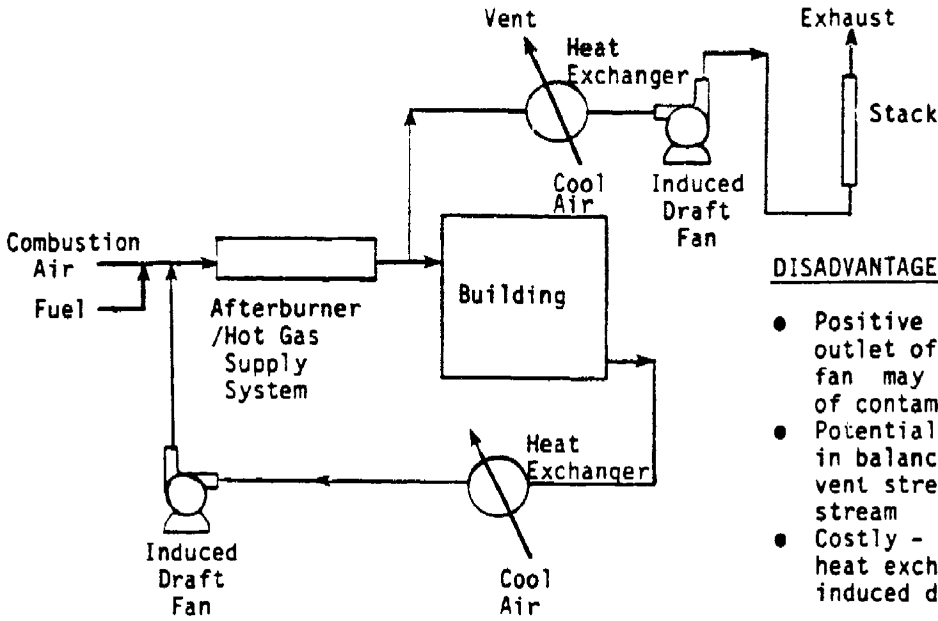
Five configurations of the hot gas decontamination system were evaluated. Two of the configurations shown in Figure 15 were not costed because of obvious disadvantages. The remaining three concepts shown in Figure 16 were further evaluated and costed. For costing, the system was segmented into the following components.

- Hot gas supply system
- Inlet Duct
- Afterburner (AFB)
- Cooling method
  - Diluent air
  - Quencher
  - Heat Exchanger
- Ductwork
- Induced Draft (ID) Fan
- Stack

These items are discussed as follows.

4.2.1 Hot Gas Supply System

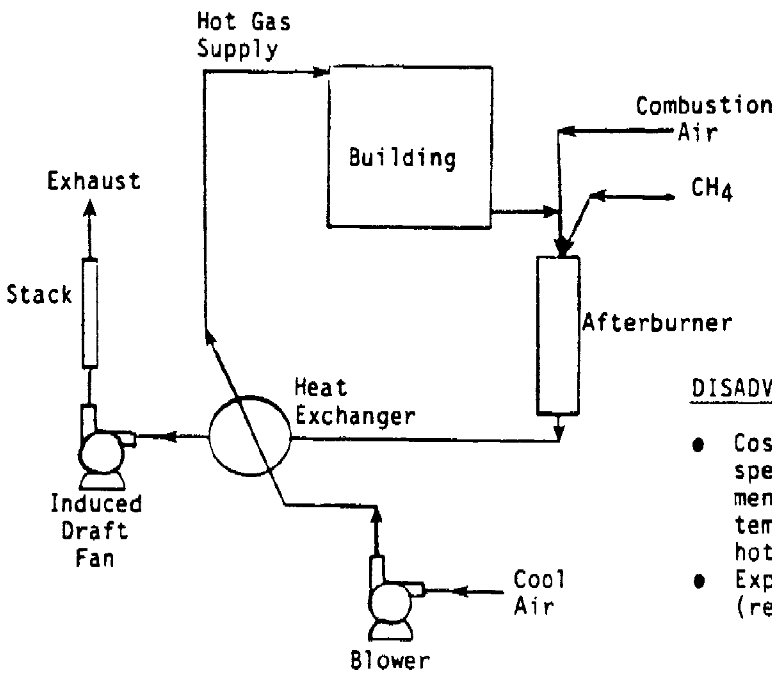
Hot gas is supplied to the building by combustion of, for example, natural gas. Other fuels such as fuel oil and propane may also be used. Diluent air is mixed with the combustion flue gas to enhance inlet gas temperature control. Calculations for a 2000 F inlet gas temperature and 1000, 2000, 3000, and 4000 scfm flow rates are as follows. It is important to note that the equipment selected from these calculations can also be used to generate 1500 F inlet gas by turndown of the burner.



DISADVANTAGES

- Positive pressure on outlet of induced draft fan may result in leakage of contaminated gas
- Potential control problems in balancing flows between vent stream and recycle stream
- Costly - requires two heat exchangers and two induced draft fans

Figure 15a



DISADVANTAGES

- Costly heat exchanger with special material requirements because of high temperature required on hot gas supply stream
- Expensive ductwork (refractory-lined) required

Figure 15b

FIGURE 15. HOT GAS APPLICATION CONCEPTS REJECTED FROM THE ENGINEERING ANALYSIS

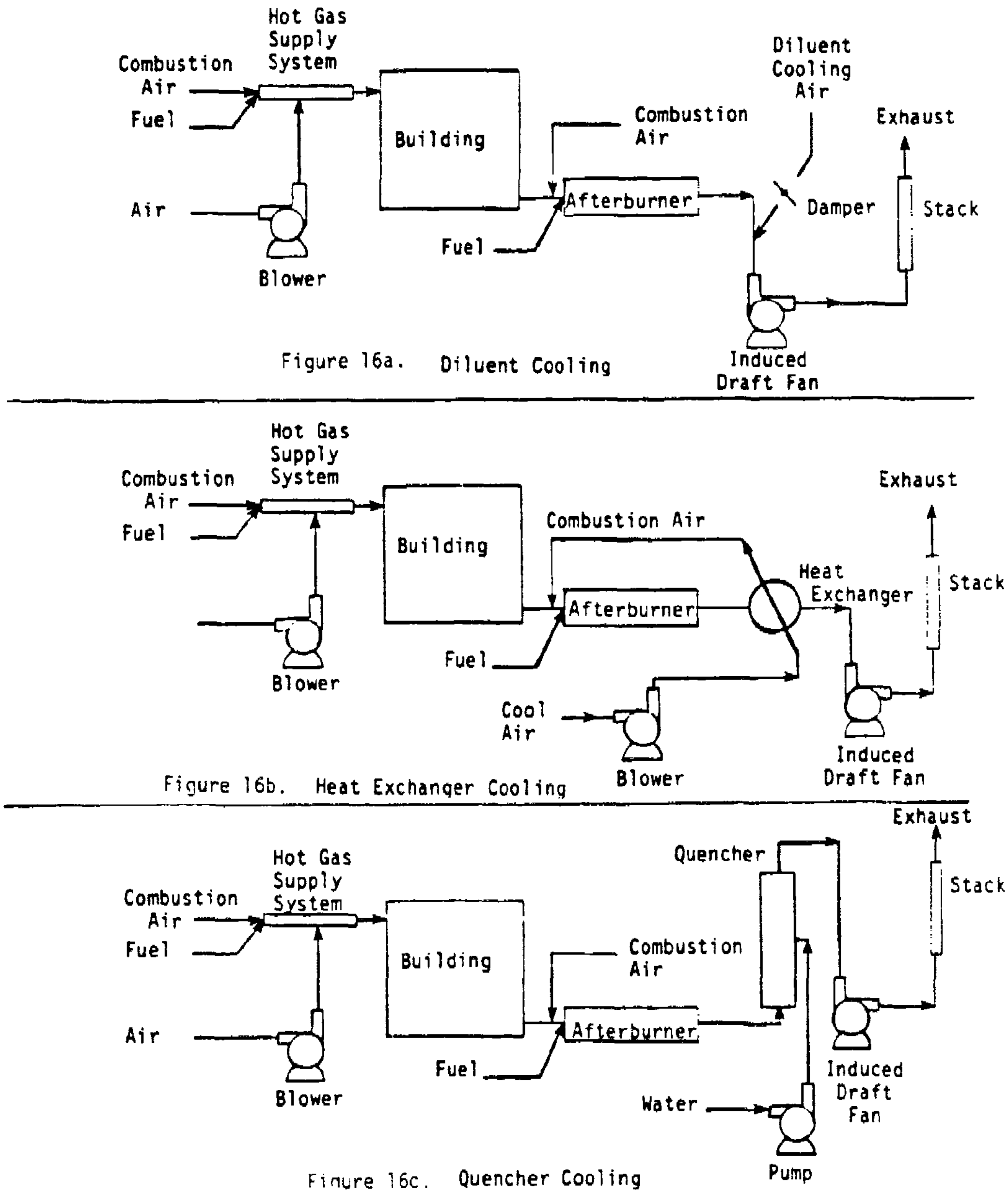


FIGURE 16. HOT GAS APPLICATION CONCEPTS SELECTED FOR ENGINEERING EVALUATION

4.2.1.1 Assumptions.

- Combustion occurs at 2000 F
- Heat of combustion of CH_4 = 23,700 Btu/lb

4.2.1.2 Calculations.

$$q_{TOTAL} = q_{AIR} \Big|_{70\ F}^{2000\ F}$$

$$q_{TOTAL} = \dot{m}_{CH_4} \text{ X heat of combustion } - q_{CH_4} \Big|_{70\ F}^{2000\ F}$$

where $\dot{m}_{CH_4}$ = methane flow rate (lb/hr)

$$q_{CH_4} \Big|_{70\ F}^{2000\ F} = \dot{m}_{CH_4} \text{ X } 15.969\text{* KCAL/gmmole X } \frac{453.6}{16} \text{ X } 3.968$$

Thus, $q_{TOTAL} = \dot{m}_{CH_4} \text{ X } 21904$
$= 58{,}573 \times v_{CH_4}$

where v = volumetric flow rate, scfm

$$q_{AIR} = \dot{m}_{AIR}\, Cp_{AIR}\, (2000-70)$$
$$= v_{AIR} \times 60 \times \frac{29}{359} \times 0.25 \times (2000-70)$$
$$= 2339 \times v_{AIR}$$

Thus, $58{,}573\ v_{CH_4} = 2339\ v_{AIR}$

Combine above equation with $v_{TOTAL} = v_{CH_4} + v_{AIR}$ to obtain v_{CH_4} and v_{AIR}. The results are given in Table 6 along with the required and selected heat duty and the flue gas composition. The selected heat duty was based on about a 50 percent excess capacity above the required heat duty to allow for contingencies. Costs for the hot gas supply system are given in Table 7.

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* From JANNAF Thermochemical Tables.

TABLE 6. HOT GAS SUPPLY MATERIAL BALANCE

v_{TOTAL} SCFM	v_{CH_4}, SCFM	v_{AIR}, SCFM	Required q, MM Btu/hr(b)	Selected q, MM Btu/hr	Flue Gas				Excess(a) O_2, %
					N_2, SCFM	H_2O, SCFM	CO_2, SCFM	O_2, SCFM	
4000	160	3840	9.4	14	3034	320	160	488	150
3000	120	2880	7.0	10	2275	240	120	365	150
2000	80	1920	4.7	7	1517	160	80	243	150
1000	40	960	2.3	4	759	80	40	122	150

(a) Excess $O_2 = 100 \times \frac{O_2 \text{ in Flue Gas (SCFM)}}{v_{CH_4} \times 2}$

(b) MM = 1,000,000.

TABLE 7. COST OF HOT GAS SUPPLY BURNER/BLOWERS

Required Heat Duty x 10^5 Btu/hr	Burner			Combustion Air Blower			Diluent Air Blower		
	Cost	Source of Cost	Type	Cost	Source of Cost	Type	Cost	Source of Cost	Type
14	$3150	1	Eclipse - Requires 38" w.c. air pressure[3]	$4000	1	2500 scfm/40 hp	$3450	1	1500 scfm/30 hp
10	$2600	2	Eclipse - Requires 38" w.c. air pressure	$3450	2	1700 scfm/30 hp	$3000	2	1300 scfm/25 hp
7	$2200	1	Eclipse - Requires 38" w.c. air pressure	$3000	2	1200 scfm/25 hp	$2500	2	800 scfm/20 hp
4	$1200	1	Eclipse - Requires 38" w.c. air pressure	$2500	1	700 scfm/20 hp	$3000	2	1300 scfm/25 hp

(1) Quote from Stelter & Brinck, Inc.
(2) Extrapolated from data obtained from (1).
(3) W.C. = Water Column.

TABLE 7. (Continued)

Burner Size x 10^6 Btu/hr	Gas Valve Train		Control Valves, etc.		Flame Control Panel		Total Cost w/o Chamber	Electrical/ Piping/ Installation @ 100% Total Cost	Total Cost
	Cost	Source	Cost	Source	Cost	Source			
14	$4250 (4" lines)	1	$1300	1	$1450	1	$17,600	$17,600	$35,200
10	$3600	2	$1300	1	$1450	1	$15,400	$15,400	$30,800
7	$2750	2	$1300	1	$1450	1	$13,200	$13,200	$26,400
4	$1900 (1¼" lines)	1	$1300	1	$1450	1	$11,350	$11,350	$22,700

(1) Quote from Stelter & Brinck, Inc.
(2) Extrapolated from data obtained from (1).

4.2.2 Inlet Duct

The burner generating the hot gas will be connected to an inlet duct which leads to the building. The purpose of the duct is to contain the open flames from the burner and to allow connection of the burner assembly to the building. The design and cost of the duct is given as follows.

4.2.2.1 Assumptions.

- 10 feet of duct
- Lined with one inch of refractory
- Hot gas velocity 3000 ft/min
- Hot gas temperature = 2000 F = 2460 R

4.2.2.2 Calculations. A refractory thickness of one inch was selected to prevent duct warpage and minimize heat losses. Heat losses are such that the hot gas temperature will drop only about 10 to 50 F through the duct. A summary of the results of the calculations and costing are given in Table 8.

4.2.3 Afterburner

Decontamination test results indicate that intact agent can be volatilized from the building during the hot gas decontamination process. As such, an afterburner (i.e., AFB) was selected to incinerate the trace quantities of agent that may be contained in the building exhaust stream.

Results of a literature search on incineration of GB, HD, and VX suggest that a 0.5 second residence time at 2000 F should achieve an agent destruction efficiency of about 99.99 percent (see Table 9). A 99.99 percent destruction efficiency should be adequate to destroy volatilized agent from a 3X building containing low concentrations of agent. If higher destruction efficiencies are required, the hot gas

TABLE 8. INLET DUCT CALCULATIONS AND COSTS

Inlet v, scfm	Inlet v, acfm	Selected ID, inches	Duct Area,(a) ft^2	Refractory Cost(b) 1984 $	Duct Cost(c) 1984 $	Total 1984 $
4000	13,566	34	89	$910	$440	$1350
3000	13,925	30	79	810	380	1190
2000	9,283	21	63	650	270	920
1000	4,642	13	47	480	220	700

(a) Duct Area = πDL

(b) 90 percent alumina firebrick = $10.25/$ft^2$ area/inch of refractory (see Chemical Engineering 2/6/84, pg. 121).

(c) 1/8" plate carbon steel duct (see Chemical Engineering 12/29/80, pg. 71-3).

TABLE 9. LITERATURE AGENT DESTRUCTION EFFICIENCIES BY INCINERATION

Agent	Temperature (F)	Residence Time (sec)	Destruction Efficiency (%)
HD(1)	1100	2.00	96.8
HD(1)	1400	1.88	99.9999
HD(2)	1472	0.14-2.22	99.9994
GB(3)	1332	0.3	99.96
GB(4)	2330	1.96	99.993
GB(4)	2337	2.14	99.9998
VX(5)	1292-1472	0.20	99.97
VX(4)	2279	2.11	99.99998
VX(4)	2546	1.73	99.99993
VX(5)	1832-2012	0.25	99.995

(1) Brooks, M. E., "Incineration/Pyrolysis of Several Agents and Related Chemical Materials Contained in Identification Sets", AD-B042888L, Oct. 1979.

(2) Sass, S., Davis, P. M., "Laboratory Research on the Incineration of Mustard", EATR-4516, May 1971.

(3) Pugh, D. L., et al., "Incineration of GB and Containment of Gaseous Products", AD-875178L, Oct. 1970.

(4) Wynne, D. J., "Pilot-Scale Incineration of GB and VX and the Containment of Gaseous Products", AD-910705L, May 1973.

(5) Hildebrandt, H. F., "Incineration of VX and Containment of Gaseous Products", AD-519538, March 1972.

flow rate can be reduced to increase the residence time of the afterburner.

The specification and cost of the afterburner are given as follows.

4.2.3.1 Assumptions.

- Combustion occurs at 2000 F
- Residence time = 0.5 sec at 2000 F
- 5 percent O_2 in the exhaust (i.e., about 30 percent excess air)
- Gas velocity of about 20 to 40 ft/sec through the chamber
- Lined with 4 inches of 90 percent alumina firebrick
- Direct fired mixing plate burner to provide mixing of the contaminated gases with combustion gas
- Heat loss through the afterburner = 10 percent of total heat duty
- Building exhaust gases at a temperature of 70 F
- Building exhaust properties similar to air

4.2.3.2 Calculations.

$$q_{TOTAL} = q_{AIR} \Big|_{70\ F}^{2000\ F} + q_{BUILDING\ EXHAUST} \Big|_{70\ F}^{2000\ F} + q_{HEAT\ LOSS}$$

$$q_{TOTAL} = 58{,}573\ v_{CH_4}{}^{*}$$

$$q_{AIR} = 2339\ v_{AIR}{}^{*}$$

$$q_{BUILDING\ EXHAUST} = v_{EXHAUST} \times 60 \times \frac{29}{354} \times 0.25 \times (2000-70)$$

$$= 2339\ v_{EXHAUST}$$

$$q_{HEAT\ LOSS} = 0.1 \times q_{TOTAL} = 5857\ v_{CH_4}$$

---

* See Hot Gas Supply System Calculations in Section 4.2.1.2.

Combining equations gives:

$$v_{CH_4} = 0.0444\,(v_{AIR} + v_{TOTAL})$$

Oxygen in afterburner exhaust = 5 percent. Therefore

$$0.05 = \frac{v_{O_2}\text{ from building} + 0.21\, v_{AIR} - 2\, v_{CH4}}{v_{TOTAL} + v_{AIR} + v_{CH_4}}$$

Combining the previous two equations gives:

$$v_{AIR} = 2.044\, v_{TOTAL} - 14.50\, v_{O_2}\text{ from building}$$

Results of the calculations are given in Tables 10A and 10B. Costs of the afterburner are given in Tables 11A and 11B.

4.2.4 Afterburner Exhaust Gas Cooling

The building must be maintained at a slight negative pressure (about minus 0.2 inches water) during the hot gas treatment to prevent volatilized agent from escaping to the atmosphere. As such, an induced draft (ID) fan is required downstream of the afterburner. The use of the ID fan will require cooling of the afterburner flue gas to below about 600 F. Three methods of cooling the flue gas are available: (1) addition of cool diluent air, (2) quenching with water, and (3) a heat exchanger. These methods are described as follows.

4.2.4.1 Diluent Air Cooling.

An illustration of the diluent air cooling method is given as follows.

TABLE 10. AFTERBURNER CALCULATIONS

TABLE 10A. AFTERBURNER MASS BALANCE

V Total, scfm	V O_2 from Building scfm	V Air scfm	V CH_4 scfm	Afterburner Flue Gas (scfm) N_2	CO_2	H_2O	O_2	Total	% O_2 in Exhaust
4000	483	1100	226	3903	335	770	267	5325	5.0
3000	365	840	170	2939	290	580	201	4010	5.0
2000	243	565	114	1963	194	388	134	2679	5.0
1000	122	275	57	976	97	194	66	1333	5.0

TABLE 10B. AFTERBURNER CHAMBER SPECIFICATION

V Total scfm	Heat Duty MM Btu/hr	Minimum Chamber Volume,(a) ft^3	Outside Chamber Diameter,(b) ft	Inside Chamber Diameter, ft	Length, ft	Inside Surface Area, ft^2	Gas Velocity, ft/sec
4000	13.24	206	5.00	4.33	14	190	28.0
3000	9.96	155	4.33	3.67	15	173	29.3
2000	6.68	104	3.67	3.00	15	141	29.3
1000	3.34	52	3.00	2.33	12.5	91	24.2

(a) Minimum chamber volume = $V_{TOTAL} \times \frac{2460}{530} \times \frac{1}{60} \times 0.5$ sec.

(b) Includes 4 inches of refractory.

TABLE 11. AFTERBURNER COSTS

TABLE 11A. AFTERBURNER CHAMBER COSTS

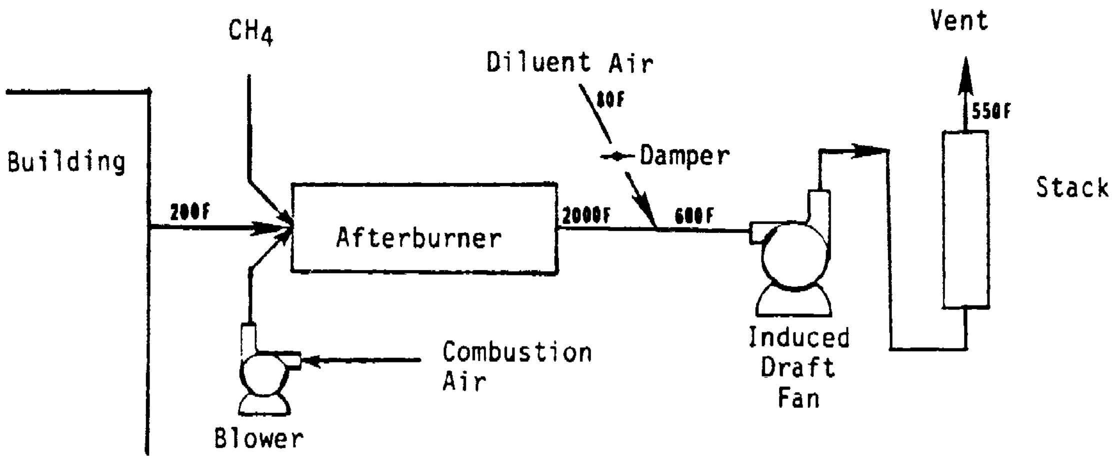
V Total, scfm	Inside Chamber Area, ft^2	Refractory Cost,[a] 1984 $	Shell Cost,[b] 1984 $	Chamber Cost, 1984 $
4000	190	$7,780	$14,250	$22,030
3000	173	7,090	12,980	20,070
2000	141	5,780	10,580	16,360
1000	91	3,730	6,830	10,560

(a) 90 percent alumina firebrick at $10.25/ft^2/inch x 4 inches (Chemical Engineering, 2/6/84, pg. 121).

(b) At $75/ft^2 area (Chemical Engineering, 2/6/84, pg. 121).

TABLE 11B. AFTERBURNER BURNER SYSTEM COSTS

Heat Duty, MM Btu/hr	Estimated Burner Cost, 1984$	Blower Size	Blower Cost, 1984 $	Gas Valve Train, 1984 $	Misc. Valves, Controls 1984 $	Total Burner System Cost, 1984 $
14	$3150	1200 scfm/ 25 hp	$3000	$4250	$3000	$10,400
10	2600	900 scfm/ 20 hp	2750	3600	3000	9,200
7	2200	700 scfm/ 20 hp	2500	2750	3000	7,950
4	1200	500 scfm/ 15 hp	2000	1900	3000	7,100



In the process the hot flue gas (T=2000 F) from the afterburner is mixed with diluent air (T=80 F) to cool the gas stream to 600 F prior to entry into the ID fan. The gas is then vented through a stack.

4.2.4.1.1 Assumptions.

- Stack gas velocity about 4000 ft/min to enhance expulsion
- Gas velocity greater than about 3000 fpm between the diluent air inlet and ID fan in order to promote turbulent mixing of the gas such that hot spots in the gas which could damage the ID fan can be minimized
- Pressure loss in the afterburner can be neglected
- Cooling air at ambient temperature of 80 F

4.2.4.1.2 Calculations. The cooling air requirements are calculated as follows.

$$q_{FLUE\ GAS} = q_{COOLING\ AIR}$$

$$v_{FLUE\ GAS} \times \frac{29\ lb}{359\ scf} \times 0.25\ Btu/lb/F \times (2000-600\ F) =$$

$$v_{COOL\ AIR} \times \frac{29\ lb}{359\ scf} \times 0.25\ Btu/lb/F \times (600-80)$$

$$v_{COOL\ AIR} = v_{FLUE\ GAS} \times 2.7$$

Results of the calculations are given in Table 12. The flow rates given in Table 12 allow the ductwork, ID fan, and stack to be specified. Because the selection of the ID fan depends not only on the volumetric gas flow rate but also on the system pressure losses, the ductwork size must be specified. The following assumptions were made for specification of the ductwork.

<u>Duct from Building to Afterburner:</u>

- Contains one elbow with a radius of 2 x diameter
- 10 ft length
- Contains one branch with a 30 degree angle of entry for injection of afterburner combustion air
- Contains one expansion joint
- Contraction loss from building to the duct is one velocity pressure (see equation on page VI-50)
- Expansion loss from duct to the afterburner in one velocity pressure
- Average gas temperature in the duct over the entire decontamination process is 200 F

<u>Duct from Afterburner to ID Fan:</u>

- Contains one branch with a 30 degree angle of entry for injection of the diluent air
- Contains one expansion joint after branch
- Duct is refractory lined from the afterburner to the branch (5 ft length)
- The duct length from the branch to the ID fan is sized to allow a 0.4 sec residence time for mixing to occur*
- Contraction loss from the afterburner to the duct is one velocity pressure
- One velocity pressure loss through damper.

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* <u>Air Pollution Engineering Manual</u>, 2nd Ed., pg. 453, May 1973.

TABLE 12. DILUENT COOLING AIR REQUIREMENTS

Hot Gas Supply, SCFM	Afterburner Combustion Gas,(a) SCFM	Afterburner Flue Gas at 2000 F, SCFM	Cooling Air Required, SCFM	Total Gas to ID Fan,(b) SCFM
4000	1325	5325	14,385	19,710
3000	1010	4010	10,830	14,840
2000	680	2680	7,230	9,910
1000	330	1330	3,590	4,920

(a) See Table 10A.
(b) At 600 F.

Duct from ID Fan to Stack:

- Contains one elbow with a radius of 2 x diameter
- 5 ft length
- Contraction loss to stack of 0.5 velocity pressures.

Stack:

- 20 ft high
- Neglect natural draft
- Gas velocity about 40 fpm

Results of the static pressure/duct specification calculations for the 2000 scfm case are given in Table 13. Similar calculations were performed for the 1000, 3000, and 4000 scfm cases. The method described in Industrial Ventilation* was used to calculate the system pressure losses along with the following equations:

$$\text{Velocity Pressure} = \left(\frac{\text{velocity (fpm)}}{4005}\right)^2$$

$$\text{Duct}\,\Delta P = \rho[\Delta Z + (4\ fL/D)(v^2/2g_c)]\times 0.19224$$

where ΔP = pressure losses, inches w.c.

ρ = gas density, lb/ft^3

f = friction factor = 0.0078 for a rough duct

L = duct length, ft

D = duct diameter, ft

V = gas velocity, ft/sec

g_c = 32.2

The ductwork specifications were then used to estimate ID fan and ductwork costs. These costs are given in Tables 14 and 15, respectively.

4.2.4.2 Quencher Cooling. An illustration of the quencher cooling method is given as follows.

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* 16th Edition, 1980.

TABLE 13. DUCTWORK SPECIFICATION - DILUENT COOLING/2000 SCFM

Item	Flow Rate, SCFM	Temp., F	Flow Rate, ACFM	Duct Diam., Inches	Veloc. FPM	Veloc. Press.	Exit/Entry Loss VPS	Exit/Entry Loss Inches w.c.	Elbow Equiv. Ft.	Branch Equiv. Ft.	Straight Duct Ft.	Total Equiv. Ft.	Duct ΔP Inches, w.c.	Total ΔP Inches, w.c.	Static ΔP Inches, w.c.
Building	-	-	-	-	-	-	-	-	-	-	-	-	-		-0.2
Duct to AFB	2000	200	2491	15	2029	0.26	2	0.52	23	15	10	48	0.25	0.77	-1.0
AFB to Branch	2680	2000	12439	30	2534	0.40	1	0.40	-	-	5	5	0.01	0.41	-1.4
Branch	7230	80	7366	24	2345	0.34	1	0.34	-	24	0	24	0.13	0.47	-1.9
Branch to ID	9910	600	19280	30	3928	0.96	-	-	-	-	26(a)	26	0.16	0.16	-2.7(b)
ID to Stack	9910	600	19280	30	3928	0.96	0.5	0.48	51	-	5	56	0.35	0.83	+1.1
Stack	9910	550	18885	30	3847	0.92	-	-	-	-	20	20	0.12	0.27(c)	+0.3

TOTAL PRESSURE LOSS = 2.7 + 1.1 = 3.8 inches w.c.

(a) 26 = 3928 fpm x 0.4/60

(b) $V_{PR} = \left[\dfrac{12439 + 7366}{\dfrac{4005 \times \pi}{4} \left[\left(\frac{30}{12}\right)^2 + \left(\frac{24}{12}\right)^2 \right]} \right]^2 = 0.38,$

Static Pressure = (-1.9 - 0.16) - (0.96 - 0.38) = -2.68

(c) Includes pressure loss for the 20 ft stack height.

TABLE 14. ID FAN SPECIFICATION/COST - DILUENT COOLING

Flow SCFM	Fan Flow ACFM	ΔP Inches w.c.	ΔP @ 600 F Inches w.c.	Fan Type	Class	Impeller Diam. In.	Fan(b) Cost 1980$	Fan(c) Dampers Cost 1980$	Required(d) Motor hp	Selected Motor hp	Motor rpm	Motor(e) Cost 1980$	Starter(f) Cost 1980$	Fan System Cost 1980$	Fan(g) System Cost 1984$
4000	39,420	4.5	9.0	Backward Curved	III	49	$8240	$3000	56	75	1200	$1800	$700	$13,740	$14,980
3000	29,680	4.0	8.0	"	III	40	6180	2300	37	50	1200	1100	450	10,030	10,930
2000	19,280	3.8	7.6	"	III	33	4635	1900	23	30	1800	500	350	7,385	8,050
1000	9,840	2.6	5.2	"	II	27	2060	1500	8	10	1800	200	200	3,960	4,320

(a) Corrected to operating temperature (see Chem. Eng. 5/18/81, pg. 171-7).

(b) CE 5/18/81. Includes 3 percent for high temperature service (250-600 F).

(c) Outlet and inlet damper.

(d) hp = v ACFM x (ΔP/12) x density of H_2O ÷ (33,000 ft/lb/min/hp x 0.5 efficiency)

(e) CE 5/18/81, pg. 171-7. Drip-proof motor.

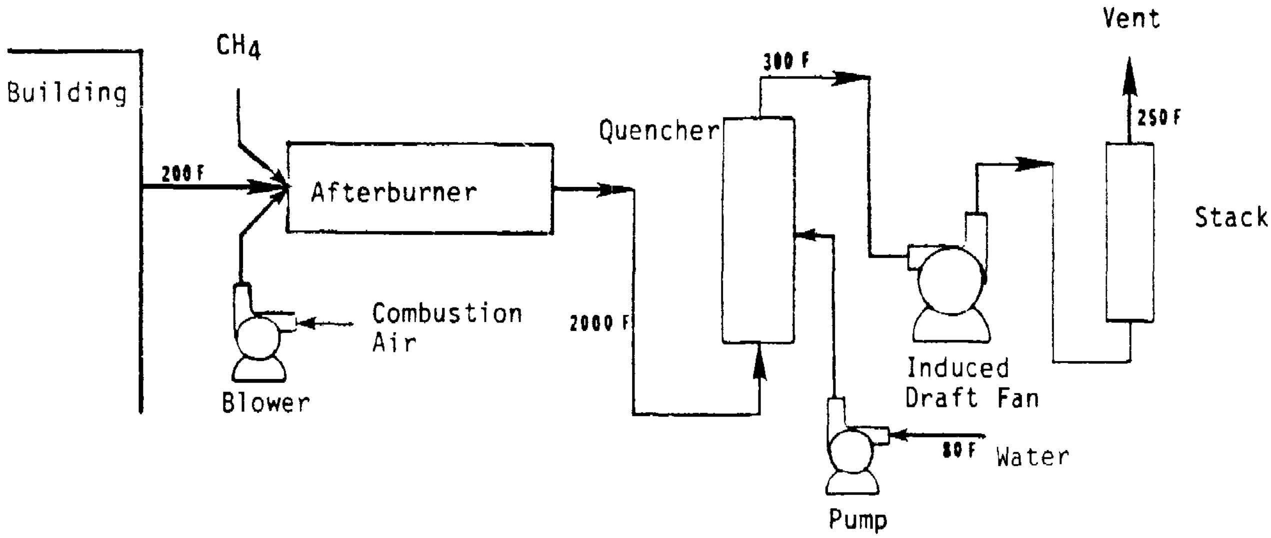
(f) Magnetic starter with circuit breaker.

(g) 1984$ = 1980$ x 1.09.

TABLE 15. DUCTWORK COSTS - DILUENT COOLING

Flow	Item	Duct ID, Ft	Duct Length, Ft	Duct[a] Cost $/Ft	Duct Cost 1980$	Refrac.[b] Cost 1980$	Elbow[a] Cost 1980$	Expan.[a] Joint Cost 1980$	Branch[a] Cost 1980$	Damper[c] Cost 1980$	Total Cost 1980$	Total Duct 1980$	Total[d] Duct 1984$
4000	Duct to AFB	2	10	25	250	-	400	2200	700	-	3550	$13,035	$14,210
	AFB to Branch	3	5	40	200	485	-	-	-	-	685		
	Branch	-	-	-	-	-	-	-	375	3100	3475		
	Branch to ID Fan	3.33	30	45	1350	-	-	3000	-	-	4350		
	ID Fan to Stack	3.33	5	45	225	-	750	-	-	-	975		
3000	Duct to AFB	1.5	10	20	200	-	300	2000	700	-	3200	$12,005	$13,085
	AFB to Branch	3	5	40	200	485	-	-	-	-	685		
	Branch	-	-	-	-	-	-	-	300	3100	3400		
	Branch to ID Fan	3	28	40	1120	-	-	2800	-	-	3920		
	ID Fan to Stack	3	5	40	200	-	600	-	-	-	800		
2000	Duct to AFB	1.25	10	20	200	-	300	1800	700	-	3000	$10,510	$11,455
	AFB to Branch	2.5	5	35	175	400	-	-	-	-	575		
	Branch	-	-	-	-	-	-	-	250	2600	2850		
	Branch to ID Fan	2.5	26	35	910	-	-	2500	-	-	3410		
	ID Fan to Stack	2.5	5	35	175	-	500	-	-	-	675		
1000	Duct to AFB	1	10	15	150	-	250	1600	700	-	2700	$ 8,620	$ 9,400
	AFB to Branch	1.67	5	20	100	270	-	-	-	-	370		
	Branch	-	-	-	-	-	-	-	200	2100	2300		
	Branch to ID Fan	2	21	25	525	-	-	2200	-	-	2725		
	ID Fan to Stack	2	5	25	125	-	400	-	-	-	525		

(a) Chemical Engineering 12/29/80, pg. 71-3. 1/8" carbon steel plate, flanges every 40 ft.
(b) One inch refractory firebrick (90 percent alumi @ $10.25/ft² inch x (π x Duct ID x L).
(c) Automatic control.
(d) 1984$ = 1980$ x (784/721.3) = 1980$ x 1.09 984$).



In the process the hot flue gas (T=2000 F) from the afterburner is quenched to a temperature of 300 F using water. The quenched gas is then directed to an ID fan and through a stack. The quencher was designed to reduce the gas stream temperature to 300 F rather than the 600 F design temperature used in the Diluent Cooling and Heat Exchanger cases (see Section 4.2.4.1 and 4.2.4.3) because of overall equipment and operational cost savings. Although the water requirements increase by one to three gpm when quenching to 300F instead of 600 F, the gas flow rate from the quencher decreases by about 1000 to 4000 acfm. A cost savings is incurred from reduction in size and power requirements of the I.D. fan, ductwork, and stack. However, an increase in water flow rate of one to three gpm would require a nominal, if any, increase in piping and pumping costs. A similar cost savings is not possible using either the Diluent Cooling or the Heat Exchanger methods.

4.2.4.2.1 Assumptions.

- Water available at 30 F
- Refractory required in duct between AFB and bottom stage of quencher

- Water flow rate is such that complete evaporation of all water entering the quencher occurs. As such, small water drops (e.g., about 100 micron diameter median size) are desirable. This requires a relatively high pressure (about 100 psig) water supply.

4.2.4.2.2 Calculations. The water requirements, assuming complete evaporation of water, are calculated as follows.

$$q_{GAS} = q_{WATER}$$

$$\dot{m}_{GAS} Cp_{GAS} \Delta T_{GAS} = \dot{m}_{WATER} \Delta H_{WATER}$$

where $Cp_{GAS} = 0.25$ BTU/lb/F

$\Delta T_{GAS} = 2000 - 300$ F

$\Delta H_{WATER} = H_{H_2O}$ at 300 F $- H_{H_2O}$ at 30 F

$= 1192 - 48 = 1144$ BTU/lb

Results of the calculations are given in Table 16.

The configuration of the quencher cooling system which was used for costing is illustrated below. A summary of the costs is given in Table 17.

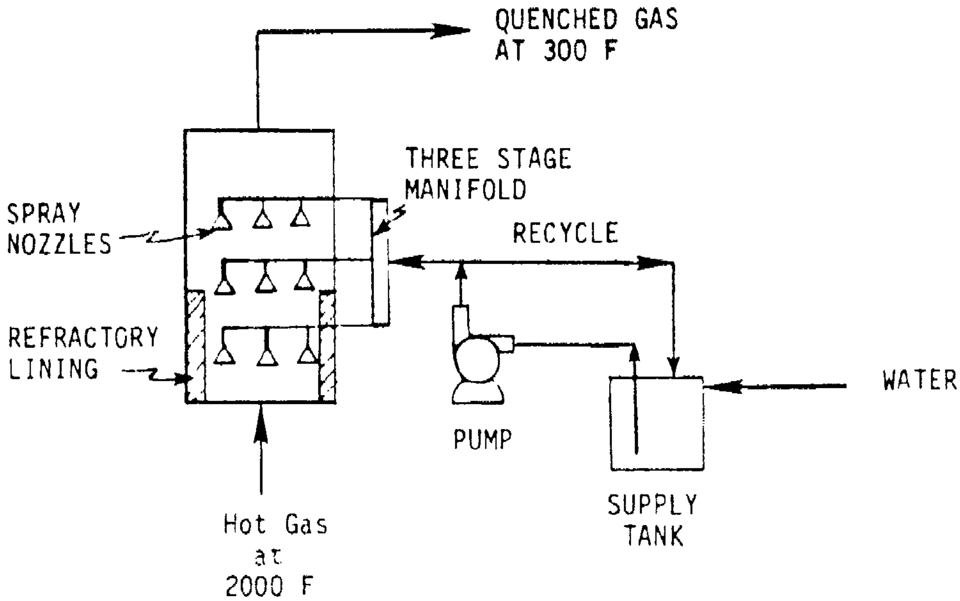


TABLE 16. QUENCHER WATER REQUIREMENTS

Hot Gas Flow, SCFM	Afterburner Flow, SCFM	Afterburner(a) Flow, lb/hr	Water Flow, lb/hr	Water Flow, gpm	Nozzles(b) Required	Quencher Output, SCFM
4000	5325	25,830	9560	19.1	18	8500
3000	4010	19,450	7200	14.4	13	6400
2000	2680	13,000	4810	9.6	9	4280
1000	1330	6,450	2390	4.8	5	2120

(a) Flow (lb/hr) = Flow (SCFM) x $\frac{29}{359}$ x 60.

(b) At a flow of about 1.1 gpm/nozzle using Spraying Systems Co. nozzle 7N-6 operating with a 100 psig supply pressure.

TABLE 17. SUMMARY OF QUENCHER COST ESTIMATES

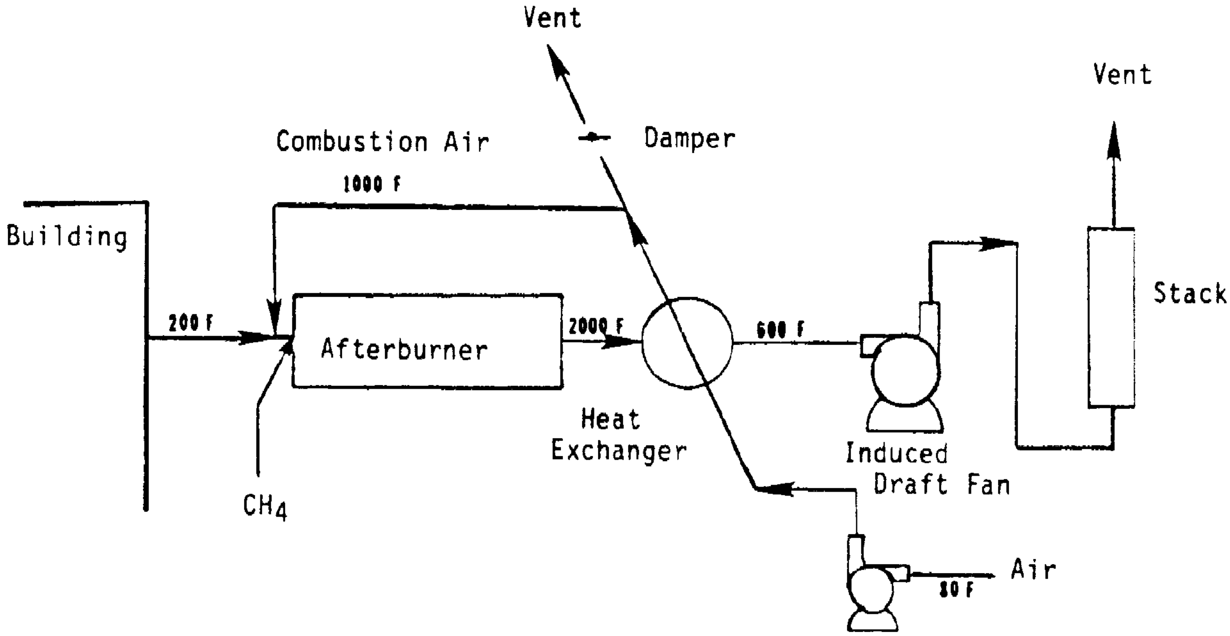
Hot Gas Supply, SCFM	Afterburner Exhaust, SCFM	Afterburner Flow,[(a)] ACFM	Quencher Cost[(b)] 1978$	Quencher Cost[(c)] 1984$	Estimated Column Height, ft	Estimated Refractory Height ft	Refractory Cost[(d)] 1984$	Pump Size,[(e)] gpm	Pump Cost,[(f)] 1984$	Water Supply Tank Cost,[(g)] 1984$	Quencher Total Cost, 1984$
4000	5325	24,700	$15,000	$21,600	17	8	$1,125	20	$2,180	$1,750	$26,700
3000	4010	18,600	13,000	18,720	15	7	860	15	2,165	1,750	23,500
2000	2680	12,400	11,000	15,840	13	6	630	10	2,165	1,750	20,400
1000	1330	6,200	8,000	11,520	10	5	350	5	2,000	1,750	15,620

(a) At 2000 F.
(b) Journal Air Pollution Control Assoc. 28, No. 9, p. 965. Includes vessel, nozzle, and supports.
(c) 1984$ = 1978$ x (783.9/545.3).
(d) 90 percent alumina firebrick at $\$10.25/\text{ft}^2/\text{inch} \times 1\ \text{inch} \times (\pi DL) \times 1.09$.
(e) Operates at 80 percent capacity, 100 psig supply pressure.
(f) Estimated by method described in Chemical Engineering, 2/22/81, pg. 115-8.
(g) 500 gallon molded polyethylene tank equipped with loose cover and stand. Cost from manufacturers brochure.

The refractory lining shown in the illustration above is required to prevent thermal damage to the quencher. Without refractory, the wall temperature can reach a temperature of about 1600 F (inlet gas = 2000 F). With one inch of refractory (k = 0.23 BTU/ft/hr/F), the wall temperature at the bottom of the quencher should not exceed about 680 F.

Ductwork specifications for the quencher system for the 2000 scfm case are given in Table 18. Similar calculations were performed for the 1000, 3000, and 4000 scfm cases. The pressure losses obtained from the ductwork specifications were then used to specify/cost an ID fan (see Table 19). Ductwork costs are given in Table 20.

4.2.4.3 Heat Exchanger. An illustration of the heat exchanger cooling method is given below.



In the process the hot flue gas (T=2000 F) from the AFB is passed through an air-cooled heat exchanger. The flue gas which exits the heat exchanger at a temperature of 600 F is directed to an ID fan and then through a stack. Because the heat recovered from the flue gas is returned to the process in the form of preheated combustion air to the AFB, the AFB energy balance must be recalculated as follows.

$$q_{COMBUSTION} = q_{AIR}\Big|_{T_{IN}}^{2000} + q_{BUILDING\ EXHAUST}\Big|_{70}^{2000} + q_{HEAT\ LOSS}$$

TABLE 18. DUCTWORK SPECIFICATION - QUENCHER/2000 SCFM

Item	Flow Rate, SCFM	Temp., F	Flow Rate, ACFM	Duct Diam., Inches	Veloc. FPM	Veloc. Press.	Exit/Entrance Loss VPS	Exit/Entrance Loss Inches w.c.	Elbow Equiv. Ft.	Branch Equiv. Ft.	Straight Duct Ft.	Total Equiv. Ft.	Duct ΔP Inches, w.c.	Total ΔP Inches, w.c.	Static ΔP Inches, w.c.
Building	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-0.2
Building to AFB	2000	200	2,490	18	1409	0.12	2	0.24	28	18	10	56	0.12	0.36	-0.6
AFB to Quencher	2680	2000	12,440	30	2534	0.40	2	0.80	51	-	10	61	0.07	0.87	-1.5
Quencher	-	-	-	-	-	-	-	-	-	-	-	-	-	1.0 (b)	-2.5
Quencher to ID	4280	300	7,070	24	2250	0.32	1	0.32	120(c)	-	15	135	0.35	0.67	-3.2
ID Fan to Stack	4280	300	7,070	24	2250	0.32	0.5	0.16	40	-	5	45	0.12	0.28	+0.9
Stack	4280	250	5,735	16	4107	1.05	-	-	-	-	20	20	0.58(a)	0.58	+0.6

(a) Includes pressure loss for the 20 ft stack height.
(b) Environmental Engineers Handbook, Volume IV, Air Pollution, B. G. Liptok, Editor, 1974.
(c) Three elbows.

Total ΔP = 3.2 + 0.9 = 4.1 inches w.c.

TABLE 19. ID FAN SPECIFICATION/COST - QUENCHER

Flow SCFM	Fan Flow ACFM	ΔP Inches w.c.	ΔP(a) @ 300 F Inches w.c.	Fan Type	Class	Impeller Diam. In.	Fan(b) Cost 1980$	Fan(c) Dampers Cost 1980$	Required(d) Motor hp	Selected Motor hp	Motor rpm	Motor(e) Cost 1980$	Starter(f) Cost 1980$	Fan System Cost 1980$	Fan(g) System Cost 1984$
4000	12,190	5.2	7.4	Backward Curved	II	27	$2060	$1500	20	25	1800	$400	$300	$4260	$4640
3000	9,180	5.5	7.9	"	II	22	1550	1300	16	20	1800	350	250	3450	3760
2000	7,070	4.1	5.9	"	II	22	1550	1300	9	10	1800	300	220	3370	3670
1000	3,040	3.4	4.9	"	I	15	600	1100	3	5	1800	150	200	2050	2230

(a) Corrected to operating temperature (see Chem. Eng. 5/18/81, pg. 171-7).
(b) CE 5/18/81. Includes 3 percent for high temp. service (250-260 F).
(c) Outlet and inlet dampers.
(d) hp = $V_{ACFM} \times \Delta P \times 3.152 \times 10^{-4}$.
(e) CE 5/18/81 for drip-proof motor.
(f) Magnetic started with circuit breaker.
(g) 1984$ = 1980$ x 1.09.

TABLE 20. DUCTWORK COSTS - QUENCHER

Flow	Item	Duct ID, Ft	Duct Length, Ft	Duct Cost $/Ft	Duct(a) Cost 1980$	Refrac.(b) Cost 1980$	Elbow Cost 1980$	Expan. Joint Cost 1980$	Branch Cost 1980$	Damper(c) Cost 1980$	Total Cost 1980$	Total Duct 1980$	Total(d) Duct 1984$
4000	Duct to AFB	2.0	10	25	250	-	400	2200	700	-	3550	$11,020	$12,010
	AFB to Quench	3.0	10	40	400	970	600	2800	-	-	4770		
	Quench to ID	2.5	15	35	525	-	3/1500	-	-	-	2025		
	ID Fan to Stack	2.5	5	35	175	-	500	-	-	-	675		
3000	Duct to AFB	1.25	10	20	200	-	300	1800	700	-	3000	$ 9,870	$10,760
	AFB to Quench	3.0	10	40	400	970	600	2800	-	-	4770		
	Quench to ID	2.0	15	25	375	-	3/1200	-	-	-	1575		
	ID Fan to Stack	2.0	5	25	125	-	400	-	-	-	525		
2000	Duct to AFB	1.5	10	20	200	-	300	1800	700	-	3000	$ 9,250	$10,080
	AFB to Quench	2.5	10	35	350	800	500	2500	-	-	4150		
	Quench to ID	2.0	15	25	375	-	3/1200	-	-	-	1575		
	ID Fan to Stack	2.0	5	25	125	-	400	-	-	-	525		
1000	Duct to AFB	1.0	10	15	150	-	250	1600	700	-	2700	$ 7,790	$ 8,490
	AFB to Quench	2.0	10	25	250	640	400	2200	-	-	3490		
	Quench to ID	1.5	15	20	300	-	3/900	-	-	-	1200		
	ID Fan to Stack	1.5	5	20	100	-	300	-	-	-	400		

(a) CE 12/29/80, pg. 71-3. 1/8" carbon steel plate, flanges every 40 ft.
(b) One inch refractory firebrick (90 percent alumina) @ $10.25/ft^2 inch x ($\pi$ x DUCT ID x L).
(c) Automatic control.
(d) 1984$ = 1980$ x 1.09.

where $q_{COMBUSTION} = v_{CH_4} \times 58573$

$q_{BUILDING\ EXHAUST} = v_{TOTAL} \times 2339$

$q_{HEAT\ LOSS} = 0.1 \times q_{COMBUSTION} = v_{CH_4} \times 5857$

$$q_{AIR} = v_{AIR} \times \frac{29}{359} \times 60 \times 0.26 \times (2000 - T_{IN})$$
$$= (2520 - 1.26 \times T_{IN})v_{AIR}$$

Combining equations gives

$$v_{CH_4} = 0.0444 v_{TOTAL} + (0.0478 - 2.39 \times 10^{-5} \times T_{IN}) \times v_{AIR}$$

Maintaining 5 percent O_2 in the afterburner flue gas gives:

$$0.05 = \frac{v_{O_2\ FROM\ BUILDING} + 0.21\ v_{AIR} - 2v_{CH_4}}{v_{TOTAL} + v_{AIR} + v_{CH_4}}$$

Combining the two equations above gives:

$$v_{AIR} = \frac{0.1445\ v_{TOTAL} - v_{O_2\ FROM\ BUILDING}}{0.065 + 4.905 \times 10^{-5} \times T_{IN}}$$

Results of the afterburner material balance calculations are given in Table 21. Modified afterburner costs are given in Table 22.

The heat exchanger area is calculated as follows.

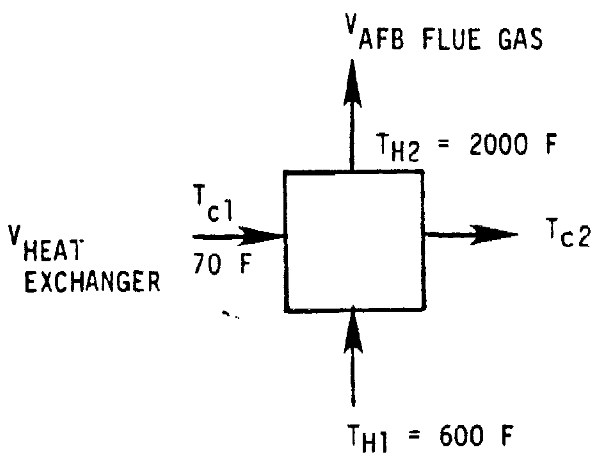


TABLE 21. AFTERBURNER MATERIAL BALANCE USING PREHEATED COMBUSTION AIR

V_{Total}, SCFM	T_{IN}, F	V_{O2} from Building, SCFM	V_{AIR}, SCFM	V_{CH4}, SCFM	V_{AFB} Flue Gas, SCFM	AFB Chamber Volume, ft^3	AFB ID, ft	AFB Length, ft	AFB Inside Area, ft^2	AFB Heat Duty, MM Btu/hr
4000	1500	488	649	192	4842	187	4.0	15.0	189	11.24
4000	1000	488	789	203	4992	193	4.0	15.5	195	11.89
4000	500	488	1005	220	5226	202	4.33	13.75	187	12.88
3000	1500	365	494	144	3639	141	3.5	14.75	162	8.43
3000	1000	365	601	153	3753	145	3.5	15.25	168	8.96
3000	500	365	765	166	3931	152	3.67	14.5	167	9.72
2000	1500	243	332	96	2428	94	3.0	13.5	127	5.62
2000	1000	243	403	102	2505	97	3.0	13.75	130	5.97
2000	500	243	514	111	2624	101	3.0	14.5	137	6.50
1000	1500	122	162	48	1210	47	2.33	11.0	81	2.81
1000	1000	122	197	51	1248	48	2.33	11.5	84	2.99
1000	500	122	251	55	1306	51	2.33	12.0	88	3.22

TABLE 22. AFTERBURNER CHAMBER COSTS FOR THE HEAT EXCHANGER SYSTEM

Hot Gas Flow, SCFM	Average Afterburner Inside Area,[(a)] ft^2	Refractory Cost,[(b)] 1984$	Shell Cost,[(c)] 1984$	Total Chamber Cost, 1984$
4000	190	$7,780	$14,250	$22,030
3000	168	6,890	12,600	19,490
2000	133	5,450	9,980	15,430
1000	84	3,440	6,300	9,740

(a) For the T_{IN} = 1000 F and T_{IN} = 500 F cases.

(b) Chemical Engineering 2/6/84 - $10.25/ft^2/inch x 4 inches.

(c) Chemical Engineering 2/6/84 - $75./ft^2.

4.2.4.3.1 Assumptions.

- Air is available at 70 F
- Overall heat transfer coefficient U = 5 BTU/ft^2/hr/F
- The temperature drop between the afterburner combustion air inlet and the heat exchanger is 150 F. Therefore, $T_{C2} = T_{IN} + 150$
- Counter-current heat exchanger.

4.2.4.3.2 Calculations. The cooling air requirements are calculated as follow:

$$q = \dot{m}_C Cp_C \Delta T_C = \dot{m}_H Cp_H \Delta T_H$$

where
$\dot{m}_C$ = cooling air flow (lb/hr)
$Cp_C = Cp_H$ = specific heat
$\dot{m}_H$ = afterburner flue gas flow (lb/hr)

$$\dot{m}_C = \dot{m}_H \frac{\Delta T_H}{\Delta T_C}$$

$$\dot{m}_C = v_{AFB\ FLUE\ GAS} \times \frac{29}{359} \times 60 \times \left(\frac{2000-600}{T_{C2}-70}\right)$$

The heat exchanger area is calculated as follows:

$$q = UA\Delta T_{LM} = \dot{m}_H\ Cp_H\,\Delta T_H$$

where
A = area (ft^2)

$$\Delta T_{LM} = \frac{(2000-TC2) - (600-70)}{\ln\left[\frac{(200-TC2)}{(600-70)}\right]}$$

Cp_H = 0.26 BTU/lb/F

Results of the calculations are given in Table 23. Costs for the heat exchanger (less air blower) were estimated as follows.

Heat Exchanger Cost = CE = $C_B F_D F_P F_M$*

Base Cost = C_B = exp (8.551-0.30863 ln(A) + 0.06811 (ln(A))^2)

For a fixed head heat exchanger:

* Chemical Engineers' Handbook, 5th Edition.

TABLE 23. HEAT EXCHANGER CALCULATIONS

$V_{HOT\ GAS}$, SCFM	V_{TOTAL}, SCFM	T_{IN}, F	T_{C2},[a] F	m_C, lb/hr	m_C, SCFM	ΔT_{LM}	A, ft^2	Heat Duty, MM Btu/hr
4000	4842	1500	1650	20796	4290	434	3939	8.54
4000	4992	1000	1150	31366	6471	677	2600	8.81
4000	5226	500	650	61144	12614	877	2103	9.22
3000	3639	1500	1650	15629	3224	434	2960	6.42
3000	3753	1000	1150	23581	4865	677	1955	6.62
3000	3931	500	650	45993	9488	877	1582	6.94
2000	2428	1500	1650	10428	2151	434	1975	4.28
2000	2505	1000	1150	15740	3247	677	1305	4.42
2000	2624	500	650	30701	6334	877	1056	4.63
1000	1210	1500	1650	5197	1072	434	984	2.14
1000	1248	1000	1150	7842	1618	677	650	2.20
1000	1306	500	650	15280	3152	877	525	2.30

(a) $T_{C2} = T_{IN} + 150$.

$F_D = \exp(-1.1156+0.0906 \ln(A))$

Pressure factor:

$F_P = 1$ (ambient pressure)

Material Factor:

$F_M = 3.8$ for Inconel or Incoloy (T=1650 to 2000 F)*

$F_M = 2.4$ for 304 SS (T is less than 1650 F)*

A summary of the costs is given in Table 24. The costs indicate that the use of either an Inconel or an Incoloy heat exchanger is cost prohibitive and, as such, are eliminated from further analyses.

Ductwork specifications for the heat exchanger system (2000 scfm case) are given, in Table 25. For the ductwork calculations, data for recycling a 1000 F air stream from the heat exchanger to the afterburner was used. Similar calculations using a 500 F air stream temperature resulted in nearly identical results. Because less combustion air than heat exchanger air is required, part of the heat exchanger air is vented to the atmosphere ("Vent" in Table 25). The pressure loss and flow rate data were then used to specify the heat exchanger blower and ID fan. Results of these estimates are given in Tables 26 and 27. Ductwork costs are given in Table 28.

4.2.5 Stack

A stack is used to aid dispersion of the hot gas exhausted from the ID fan. Because of the incineration step upstream of the stack, pollutant dispersion from the stack exhaust is probably not required. As a preliminary estimate a 20 foot high carbon steel stack was selected. A summary of the stack costs for the various hot gas methods are given in Table 29.

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* See Chemical Engineering, 1/25/82, 125-6.

TABLE 24. HEAT EXCHANGER COSTS

$V_{HOT\ GAS}$, SCFM	T_{IN}, F	Area, ft^2	C_B, 1981$	F_D	Material Type	CE, 1981$	CE,* 1984$
4000	1500	3939	$42,786	0.694	INCONEL	$112,808	$122,959
4000	1000	2600	30,806	0.668	304 S.S.	49,402	53,848
4000	500	2103	26,285	0.655	304 S.S.	41,350	45,072
3000	1500	2960	34,047	0.676	INCONEL	87,470	95,343
3000	1000	1955	24,924	0.651	304 S.S.	38,950	42,456
3000	500	1582	21,449	0.639	304 S.S.	32,883	35,843
2000	1500	1975	25,109	0.652	INCONEL	62,185	67,782
2000	1000	1305	18,812	0.628	304 S.S.	28,341	30,891
2000	500	1056	16,379	0.616	304 S.S.	24,206	26,385
1000	1500	984	15,660	0.612	INCONEL	36,420	39,580
1000	1000	650	12,200	0.589	304 S.S.	17,245	18,800
1000	500	525	10,830	0.578	304 S.S.	15,020	16,375

* 1984$ = 1981$ x 783.9/721.3

TABLE 25. DUCTWORK SPECIFICATION - HEAT EXCHANGER/2000 SCFM

Item	Flow Rate, SCFM	Temp., F	Flow Rate, ACFM	Duct Diam., Inches	Veloc. FPM	Veloc. Press.	Exit/Entrance Loss		Elbow Equiv. Ft.	Branch Equiv. Ft.	Straight Duct Ft.	Total Equiv. Ft.	Duct ΔP Inches, w.c.	Total ΔP Inches, w.c.	Static ΔP Inches, w.c.
							VPS	Inches w.c.							
Building	-	-	-	-	-	-	-	-	-	-	-	-	-		-0.2
Duct to Branch	2000	200	2491	15	2029	0.26	1	0.26	23	-	10	33	0.17	0.43	-0.6
Branch	2403	334	3601	18	2037	0.26	1	0.26	-	18	2	20	0.07	0.33	-0.8[(a)]
Heat Exchanger	-	-	-	-	-	-	-	-	-	-	-	-	-	4.0	-4.8
HE to ID	2505	600	5010	18	2835	0.50	0	-	-	-	5	5	0.03	0.03	-4.8
ID to Stack	2505	600	5010	18	2835	0.50	0.5	0.25	28	-	5	33	0.17	0.42	+0.9
Stack	2505	500	4537	14	4244	1.12	0	-	-	-	20	20	0.49	0.49	+0.5
H.E. to Vent	3247	1150	9864	24	3139	0.61	0	-	-	24	5	29	0.09	0.09	+0.4
Recycle	403	1000	1110	10	2035	0.26	0	-	42	-	30	72	0.25	0.25	+0.3
Vent	2844	1150	8639	24	2750	0.47	0.5	0.24	-	-	10	10	0.02	0.26	-

(a) $V_{PR} = \left\{ \dfrac{3601}{\dfrac{4005\,\pi}{4}\left[\left(\dfrac{15}{12}\right)^2 + \left(\dfrac{10}{12}\right)^2\right]} \right\}^2 = 0.51.$

ID Fan ΔP = 4.8 = 0.9 = 5.7" w.c.
H.E. Fan ΔP = 4.0 (Heat Exc) + 0.4 = 4.4" w.c.

Static Pressure = (0.6 + 0.33) - (0.26 - 0.51) = 0.8.

TABLE 26. HEAT EXCHANGER FAN SPECIFICATION/COST

Flow SCFM	Fan Flow ACFM	ΔP Inches w.c.	Corrected(a) ΔP Inches w.c.	Fan Type	Class	Impeller Diam. In.	Fan(b) Cost 1980$	Fan(c) Dampers Cost 1980$	Required(d) hp	Selected Motor hp	Motor rpm	Motor(e) Cost 1980$	Starter(f) Cost 1980$	Fan System Cost 1980$	Fan(g) System Cost 1984$
4000/ 1000 F	6471	4.5	4.5	Backward Curved	I	22	$1200	$1300	9.2	10	1800	$200	$200	$2900	$3160
3000/ 1000 F	4365	4.4	4.4	"	I	18	800	1200	6.7	7.5	1800	200	200	2400	2620
2000/ 1000 F	3247	4.4	4.4	"	I	15	600	1000	4.5	5	1800	150	200	1950	2130
1000/ 1000 F	4915	5.3	5.3	"	II	18	1000	1200	8.2	10	1800	200	200	2600	2830

(a) Corrected to operating temperature (see Chem. Eng., 5/18/81, pg. 171-7).
(b) CE 5/18/81.
(c) Outlet and inlet damper.
(d) hp = $V_{ACFM} \times \Delta P \times 3.152 \times 10^{-4}$.
(e) Drip-proof motor.
(f) Magnetic starter with circuit breaker.
(g) 1984$ = 1980$ x 1.09.

TABLE 27. ID FAN SPECIFICATION/COST - HEAT EXCHANGER

Flow SCFM	Fan Flow ACFM	ΔP Inches w.c.	Corrected[a] ΔP Inches w.c.	Fan Type	Class	Impeller Diam. In.	Fan[b] Cost 1980$	Fan[c] Dampers Cost 1980$	Required[d] hp	Selected Motor hp	Motor rpm	Motor[e] Cost 1980$	Starter[f] Cost 1980$	Fan System Cost 1980$	Fan[g] System Cost 1984$
4000	10,000	5.9	11.8	Backward Curved	III	22	$2575	$1300	18.6	20	3600	$500	$250	$4625	$5040
3000	7,500	5.9	11.8	"	III	18	1850	1200	13.9	15	3600	300	250	3600	3920
2000	5,000	5.7	11.4	"	III	15	1545	1000	9.0	10	3600	200	200	2945	3210
1000	2,500	6.3	12.6	"	III	12	1200	800	5.0	7.5	3600	200	150	2350	2560

(a) Corrected to operating temperature (see Chem. Eng., 5/18/81, pg. 171-7).
(b) CE 5/18/81. Includes 3 % for high temperature service (250-600 F).
(c) Outlet and inlet damper.
(d) hp = $V_{ACFM} \times \Delta P \times 3.152 \times 10^{-4}$.
(e) Drip-proof motor.
(f) Magnetic starter with circuit breaker.
(g) 1984$ = 1980$ x 1.09.

TABLE 28. DUCTWORK COSTS - HEAT EXCHANGER SYSTEM

Flow	Item	Duct ID, Ft	Duct Length, Ft	Duct Cost $/Ft	Duct Cost 1980$	Refrac. Cost 1980$	Elbow Cost 1980$	Expan. Joint Cost 1980$	Branch Cost 1980$	Damper Cost 1980$	Total Cost 1980$	Total Duct 1980$	Total Duct 1984$
4000	ID System	2	22	25	550	-	900	2200	700	-	4250		
	H.E. Vent	3	15	40	600	-	-	-	300	3500	4400	$11,450	$12,480
	Recycle	1	30	15	450	-	750	1600	-	-	2800		
3000	To Branch	1.5	10	20	200	-	300	2000	-	-	2500		
	ID System	2	12	25	300	-	400	-	700	-	1400	$10,575	$11,530
	H.E. Vent	2.5	15	35	525	-	-	-	250	3100	3875		
	Recycle	1	30	15	450	-	750	1600	-	-	2800		
2000	To Branch	1.25	10	20	200	-	300	1800	-	-	2300		
	ID System	1.5	12	20	240	-	300	-	700	-	1240	$ 8,815	$ 9,610
	H.E. Vent	2.0	15	25	375	-	-	-	200	2600	3175		
	Recycle	0.83	30	10	300	-	600	1200	-	-	2100		
1000	To Branch	1	10	15	150	-	250	1600	-	-	2000		
	ID System	1	12	15	180	-	250	-	700	-	1130	$ 6,980	$ 7,610
	H.E. Vent	1.5	15	20	300	-	-	-	150	2000	2450		
	Recycle	0.5	30	5	150	-	450	800	-	-	1400		

TABLE 29. STACK COSTS

Flue Gas Cooling Method	Hot Gas Flow Rate, SCFM	Stack Flow, ACFM	Stack ID, Inches	Stack[(a)] Cost, 1977$	Stack[(b)] Cost 1984$
Diluent Air	4000	37,560	40	$ 2300	$ 3565
Diluent Air	3000	28,280	36	2100	3255
Diluent Air	2000	18,885	30	2000	3100
Diluent Air	1000	9,380	20	1600	2480
Quencher	4000	11,390	22	1700	2635
Quencher	3000	8,575	20	1600	2480
Quencher	2000	7,515	18	1500	2325
Quencher	1000	2,840	12	1000	1550
Heat Exchanger	4000	9,000	20	1600	2480
Heat Exchanger	3000	6,800	18	1500	2325
Heat Exchanger	2000	4,540	14	1200	1860
Heat Exchanger	1000	2,261	10	-	1500[(c)]

(a) Journal Air Poll. Control Assoc. V28, No. 9, p. 963-8, 1978. For a carbon steel stack, 1/4-inch plate. Includes flange, stack, four stainless steel cables, clamps, and surface coating.

(b) 1984$ = 1978$ x 783.9/505.4 (3rd Quarter 1984$). See Chemical Engineering 11/26/84, pg. 7.

(c) Estimated.

4.3 Hot Gas Decontamination Cost Summary

4.3.1 Capital Costs

A summary of capital costs for the 1000, 2000, 3000, and 4000 SCFM cases are given in Tables 30 through 33, respectively.

4.3.2 Operating Costs

Heat transfer calculations indicate that the buildings being decontaminated must be insulated in order to heat all areas to a temperature of 300 F. These calculations (see Tables 3 through 5) assumed an insulation thickress of 2, 4 and 12 inches and a thermal conductivity of 0.05 Btu;ft/hr/F (R=40, 80 and 120, respectively). These were selected as typical values which would provide a basis for determination of the effect of insulation on heat transfer. For costing purposes foil faced, non-rigid, Fiberglas blanket (6 inch x 23 inch-wide roll with R=19) was selected. In order to achieve R values of 40, 80 and 120, either 2, 4, or 12 layers of this insulation is required. Costs for the insulation are given, as follows:

Layers	R	Material Cost 1984$/ft^2	Installation* Cost 1984$/ft^2	Total Cost 1984$/ft^2
2	40	$0.56	$0.20	$0.76
4	80	1.12	0.40	1.52
12	240	3.36	1.20	4.56

Other types of insulation with conductivities closer to 0.05 BTU/ft/hr/F may be used; however, the material cost would be higher, the installation cost would be lower, and the total cost may be slightly higher than for the insulation specified above.

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* Costs derived from data in Building Construction Cost Data, 42nd Edition, 1984.

TABLE 30. SUMMARY OF CAPITAL COSTS (1000 SCFM/4 MM Btu/Hr Case)

Item	Size	Diluent Air	Quencher	Heat Exchanger
Hot Gas Supply	4 MM Btu/Hr/1000 SCFM	$ 11,400	$ 11,400	$ 11,400
Inlet Duct	18" ID/10 ft/1" refractory	700	700	700
Afterburner System	4 MM Btu/Hr	7,100	7,100	7,100
Afterburner Chamber	1300 SCFM/2000 F/0.5 sec	10,600	10,600	9,700
ID Fan	10 hp/3"/4900 SCFM	4,300	-	-
"	5 hp/3"/3000 SCFM	-	2,200	-
"	7.5 hp/6"/1250 SCFM	-	-	2,600
Ductwork	Carbon steel/12 to 24" ID	9,400	-	-
"	Carbon steel/12 to 24" ID	-	8,500	-
"	Carbon steel/6 to 12" ID	-	-	7,600
Stack	20" ID/20 ft ht	2,500	-	-
"	12" ID/20 ft ht	-	1,600	-
"	10" ID/20 ft ht	-	-	1,500
Quencher	6,200 ACFM/4.8 gpm	-	15,600	-
Heat Exchanger/Fan	304 S.S./650 ft^2/1000 F/4900 SCFM	-	-	21,600
Sampling/Miscellaneous		15,000	15,000	15,000
	Purchased Equipment Cost (PEC)	$ 61,000	$ 72,700	$ 77,200
	Installation (50% of PEC), Instrumentation and Controls, (15% of PEC), Piping (10% of PEC) and Electrical (25% of PEC)	61,000	72,700	77,200
	Total Capital Cost	$122,000	$145,400	$154,400

TABLE 31. SUMMARY OF CAPITAL COSTS (2000 SCFM/7 MM Btu/Hr Case)

Item	Size	Diluent Air	Quencher	Heat Exchanger
Hot Gas Supply	7 MM Btu/Hr/2000 SCFM	$ 13,200	$ 13,200	$ 13,200
Inlet Duct	30" ID/10 ft/1" refractory	900	900	900
Afterburner System	7 MM Btu/Hr/1200 SCFM	8,000	8,000	8,000
Afterburner Chamber	2700 SCFM/2000 F/0.5 sec	16,400	16,400	15,400
ID Fan	30 hp/4" H_2O/20,000 SCFM	8,100	-	-
"	15 hp/5" H_2O/5600 SCFM	-	3,700	-
"	10 hp/6" H_2O/2500 SCFM	-	-	3,200
Ductwork	Carbon steel/15 to 30" ID	11,500	-	-
"	Carbon steel/18 to 30" ID	-	10,100	-
"	Carbon steel/10 to 24" ID	-	-	9,600
Stack	30" DIAM/20 ft ht	3,100	-	-
"	22" DIAM/20 ft ht	-	2,300	-
"	14" DIAM/20 ft ht	-	-	1,900
Quencher	12,400 ACFM/9.6 gpm	-	20,400	-
Heat Exchanger/Fan	304 S.S./1305 ft^2/1000 F/6500 SCFM	-	-	33,000
Sampling/Miscellaneous		15,000	15,000	15,000
	Purchased Equipment Cost (PEC)	$ 76,200	$ 90,000	$100,200
	Installation (50% of PEC), Instrumentation and Controls, (15% of PEC), Piping (10% of PEC) and Electrical (25% of PEC)	76,200	90,000	100,200
	Total Capital Cost	$152,400	$180,000	$200,400

TABLE 32. SUMMARY OF CAPITAL COSTS (3000 SCFM/10 MM Btu/Hr Case)

Item	Size	Diluent Air	Quencher	Heat Exchanger
Hot Gas Supply	10 MM Btu/Hr/3000 SCFM	$ 15,400	$ 15,400	$ 15,400
Inlet Duct	30" ID/10 ft/1" refractory	1,200	1,200	1,200
Afterburner System	10 MM Btu/Hr/900 SCFM	9,200	9,200	7,700
Afterburner Chamber	4000 SCFM/2000 F/0.5 sec	20,100	20,100	19,500
ID Fan	50 hp/4" H_2O/30,000 SCFM	10,900	-	-
"	20 hp/6" H_2O/5600 SCFM	-	3,800	-
"	10 hp/6" H_2O/3750 SCFM	-	-	3,900
Ductwork	Carbon steel/18 to 36" ID	13,100	-	-
"	Carbon steel/15 to 36" ID	-	10,800	-
"	Carbon steel/12 to 30" ID	-	-	11,500
Stack	36" DIAM/20 ft ht	3,300	-	-
"	20" DIAM/20 ft ht	-	2,500	-
"	18" DIAM/20 ft ht	-	-	2,300
Quencher	18,600 ACFM/14.4 gpm	-	23,500	-
Heat Exchanger/Fan	304 S.S./1955 ft^2/1000 F/4900 SCFM	-	-	45,100
Sampling/Miscellaneous		15,000	15,000	15,000
	Purchased Equipment Cost (PEC)	$ 88,200	$101,500	$121,600
	Installation (50% of PEC), Instrumentation and Controls, (15% of PEC), Piping (10% of PEC) and Electrical (25% of PEC)	88,200	101,500	121,600
	Total Capital Cost	$176,400	$203,000	$243,200

TABLE 33. SUMMARY OF CAPITAL COSTS (4000 SCFM/14 MM Btu/Hr Case)

Item	Size	Diluent Air	Quencher	Heat Exchanger
Hot Gas Supply	14 MM Btu/Hr/4000 SCFM	$ 17,600	$ 17,600	$ 17,600
Inlet Duct	36" ID/10 ft/1" refractory	1,400	1,400	1,400
Afterburner System	14 MM Btu/Hr/1200 SCFM	10,400	10,400	10,400
Afterburner Chamber	5300 SCFM/2000 F/0.5 sec	22,000	22,000	22,000
ID Fan	75 hp/4.5"/40,000 SCFM	15,000	-	-
"	25 hp/5.2"/12,200 SCFM	-	4,600	-
"	20 hp/5.9"/5000 SCFM	-	-	5,000
Ductwork	Carbon steel/24 to 40" ID	14,200	-	-
"	Carbon steel/24 to 36" ID	-	12,000	-
"	Carbon steel/12 to 36" ID	-	-	12,500
Stack	40" DIAM/20 ft ht	3,600	-	-
"	22" DIAM/20 ft ht	-	2,600	-
"	20" DIAM/20 ft ht	-	-	2,500
Quencher/Pump	24,700 ACFM/19.1 gpm	-	26,700	-
Heat Exchanger/Fan	304 S.S./2600 ft^2/1000 F/6500 SCFM	-	-	57,000
Sampling/Miscellaneous		15,000	15,000	15,000
	Purchased Equipment Cost (PEC)	$ 99,200	$112,300	$143,400
	Installation (50% of PEC), Instrumentation and Controls, (15% of PEC), Piping (10% of PEC) and Electrical (25% of PEC)	99,200	112,300	143,400
	Total Capital Cost	$198,400	$224,600	$286,800

For costing, it was assumed that the insulation can be re-used for the three buildings thereby allowing a cost savings on materials. Insulation removal costs were assumed to be identical to the installation cost.

A reduction in the potential for agent release can be achieved if a vapor barrier (i.e., 10 mil polyethylene sheet) is installed over the insulation on each building being decontaminated. Placement of the plastic vapor barrier on the cool side of the insulation would minimize the potential for melting. Calculations show that the vapor barrier temperature should not exceed 82 or 93 F for insulation with R values of 120 and 40, respectively.* The cost of the vapor barrier was estimated at $6.00/100 sq.ft. for material** and $4.16/100 sq.ft for installation** for a total of $10.16/100 sq.ft. Caulk/joint sealant can be used to seal cracks, etc. as required to minimize leakage into the building. Sealant was estimated at a cost of $1.26/linear foot.** It was also assumed that external concrete surfaces exposed to the atmosphere would be coated with a decontaminant such as STB or DPAB to minimize the potential for agent release. The cost for application of the coating is not included in the building preparation costs.

In Building 1, the top structure composed of wood will be removed prior to decontamination leaving a concrete basement without a ceiling. As such, a steel deck must be erected to serve as support for the insulation. Cost estimates** for the steel deck are given below. Because the wood will be removed for any decontamination concept, the costs for removal and incineration were not included in the cost.

Layers	Load,*** PSF	Material Cost, 1984$/ft^2	Installation Cost, 1984$/ft^2	Total Deck Cost, 1984$/ft^2
2	20	$2.20	$0.88	$3.08
4	40	2.56	1.03	3.59
12	120	8.96	1.35	10.31

* Assumes a 300 F wall temperature, an 80 F air temperature, and h = 4.6 BTU/ft^2/hr/F.

** Costs derived from data in Building Construction Cost Data, 42nd Edition, 1984.

*** Insulation density = 20 lb/ft^3.

In addition to the building preparation costs detailed above, it is estimated that two personnel working two weeks at 40 hours per week are required to install the skid-mounted equipment and perform the necessary utility connections.

A summary of the building preparation costs for the three buildings is given in Table 34. Operating costs for decontamination were estimated using the building preparation costs along with utility costs (natural gas and electricity), operator cost and clean-up costs. The following assumptions were made in estimating these costs:

- Natural gas is available at $4.04/SCF (Energy User News 11/19/84).
- Electricity is available at $0.0524/kWh (Energy User News 11/19/84).
- Afterburner natural gas requirements for the three cooling methods are essentially the same.*
- Three operators at $28.45/hr each are required to operate the equipment**.
- One engineer/foreman is required at $35.00 per hour**.
- One week is required for equipment teardown at each building (2 operators at 40 hours/week).
- The cost to remove the insulation, steel deck, and vapor barrier is identical to the installation cost.
- A 65 percent motor electrical efficiency is assumed.
- Hot gas supply, afterburner, and miscellaneous controls require 30 kva.

A summary of the operating costs for Buildings 1, 2, and 3 are given in Tables 35, 36, and 37, respectively.

4.3.3 Cost Summary

A summary of the operating and capital costs of the hot gas concept for the various flow rates, insulation thickness, and

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* The afterburner natural gas costs were approximately 10 percent higher for the diluent air and quencher methods than the heat exchanger method.

** Building Construction Cost Data, 42nd Ed., 1984. Includes overhead and profit.

TABLE 34. SUMMARY OF BUILDING PREPARATION COSTS

Building Number	Insulation Thickness, Inches	Surface Area Requiring Insulation, ft^2	Insulation Cost, 1984$	Steel Deck Cost, 1984$	Vapor Barrier, 1984$	Joint Sealant, 1984$	Install Skids, 1984$	Total Building Preparation, 1984$
1	2	10,500(a)	$ 7,980	$ 32,300	$1070	-	$ 4550(b)	$ 45,900
1	4	10,500(a)	15,960	37,700	1070	-	4550(b)	59,280
1	12	10,500(a)	47,880	108,300	1070	-	4550(b)	161,800
2	2	17,600	7,500(c)	-	1780	1260	4550(b)	15,090
2	4	17,600	14,990(c)	-	1780	1260	4550(b)	22,580
2	12	17,600	44,980(c)	-	1780	1260	4550(b)	52,570
3	2	11,000	1,100(d)	-	1120	630	4550(b)	8,500
3	4	11,000	4,400(d)	-	1120	630	4550(b)	10,700
3	12	11,000	13,200d)	-	1120	630	4550(b)	19,500

(a) $150 \times 70 = 10{,}500$ ft^2.
(b) Building Construction Cost Data, 1984 gives a skilled laborer average charge rate (including overhead and profit) as $28.45/hr. Thus, $28.45/hr x 40 hr/week x 2 weeks x 2 people = $4550.
(c) Includes credit for re-use of insulation from Building 1.
(d) Includes credit for re-use of insulation from Building 2.

TABLE 35. OPERATING COSTS FOR BUILDING 1

Hot Gas Flow SCFM	T_{IN} F	Insul., Inches	Decon. Time, Hrs	Hot Gas Supply CH_4 1000 SCF	Hot Gas CH_4, 1984$	Afterburner CH_4, 1984$	Electricity KVA	Electricity 1984$	Operators, 1984$	Bldg. Prep., 1984$	Cleanup(a) 1984$	Total 1984$
1000	2000	2	138	444	$1790	$1910	110	$800	$ 16,610	$45,900	$16,290	$ 83,300
1000	2000	4	111	357	1450	1530	110	640	13,360	59,280	21,690	97,950
1000	2000	12	98	315	1270	1350	110	560	11,790	151,800	31,790	208,560
2000	2000	2	58	328	1330	1600	139	420	6,980	45,900	16,290	72,520
2000	2000	4	53	300	1210	1460	139	390	6,380	59,280	21,690	90,410
2000	2000	12	50	283	1140	1380	139	360	6,020	161,800	31,790	202,490
3000	2000	2	40	330	1330	1650	173	360	4,810	45,900	16,290	70,340
3000	2000	4	37	305	1230	1520	173	340	4,450	59,280	21,690	88,510
3000	2000	12	36	297	1200	1490	173	330	4,330	161,800	31,790	200,930
4000	2000	2	31	336	1360	1700	225	370	3,730	45,900	16,290	69,350
4000	2000	4	30	325	1310	1640	225	350	3,610	59,280	21,690	87,880
4000	2000	12	29	314	1270	1590	225	340	3,490	161,800	31,790	200,280

(a) Remove steel deck, insulation, vapor barrier, and decontamination equipment.

TABLE 36. OPERATING COSTS FOR BUILDING 2

Hot Gas Flow SCFM	T_{IN} F	Insul., Inches	Decon.[a] Time, Hrs	Hot Gas Supply CH_4 1000 SCF	Hot Gas CH_4, 1984$	Afterburner CH_4, 1984$	Electricity KVA	Electricity 1984$	Operators, 1984$	Bldg. Prep., 1984$	Cleanup[b] 1984$	Total 1984$
1000	2000	2	483	1192	$5990	$6670	110	$2780	$ 58,130	$15,090	$ 8,070	$ 96,730
1000	2000	4	366	1125	4550	5060	110	2110	44,050	22,580	11,590	89,940
1000	2000	12	309	948	3830	4270	110	1780	37,190	52,570	25,670	125,310
2000	2000	2	285	1614	6520	7880	139	2080	34,300	15,090	8,070	73,940
2000	2000	4	237	1341	5420	6550	139	1730	28,520	22,580	11,590	76,340
2000	2000	12	210	1198	4800	5800	139	1530	25,270	52,570	25,670	115,640
3000	2000	2	222	1833	7410	9150	173	2010	26,720	15,090	8,070	68,450
3000	2000	4	192	1584	6400	7910	173	1740	23,110	22,580	11,590	73,330
3000	2000	12	174	1437	5810	7170	173	1580	20,940	52,570	25,670	113,740
4000	2000	2	192	2082	8410	10520	225	2260	23,110	15,090	8,070	67,460
4000	2000	4	168	1921	7360	9200	225	1980	20,220	22,580	11,590	72,930
4000	2000	12	153	1659	6700	8390	225	1800	18,410	52,570	25,670	113,540

(a) For 3 stories.
(b) Remove vapor barrier, insulation, and decontamination equipment.

TABLE 37. OPERATING COSTS FOR BUILDING 3

Hot Gas Flow SCFM	T_{IN} F	Insul., Inches	Decon. Time, Hrs	Hot Gas Supply CH_4 1000 SCF	Hot Gas CH_4, 1984$	Afterburner CH_4, 1984$	Electricity KVA	Electricity 1984$	Operators, 1984$	Bldg. Prep., 1984$	Cleanup[a] 1984$	Total 1984$
1000	2000	2	52	167	$ 670	$ 720	110	$ 300	$ 6260	$ 8,500	$ 6,750	$ 23,200
1000	2000	4	51	126	510	700	110	290	6140	10,700	8,950	27,290
1000	2000	12	36	116	470	500	110	210	4330	19,500	17,750	42,760
2000	2000	2	27	153	620	750	139	200	3250	8,500	6,750	20,070
2000	2000	4	24	136	550	660	139	170	2890	10,700	8,950	23,920
2000	2000	12	23	130	530	640	139	170	2770	19,500	17,750	41,360
3000	2000	2	20	165	670	820	173	180	2410	8,400	6,750	19,330
3000	2000	4	19	157	630	780	173	170	2290	10,700	8,950	23,570
3000	2000	12	18	149	600	740	173	160	2170	19,500	17,750	40,920
4000	2000	2	17	184	740	930	225	200	2050	8,500	6,750	19,170
4000	2000	4	15	173	700	880	225	190	1930	10,700	8,950	23,350
4000	2000	12	16	173	700	880	225	190	1930	19,500	17,750	40,950

(a) Remove vapor barrier, insulation, and decontamination equipment.

afterburner flue gas cooling methods is given in Table 38. The results are also shown in Figure 17. The following conclusions may be drawn:

- Total costs increase with an increase in hot gas flow rate over the range of 1000 to 4000 scfm.
- Total costs increase with an increase in insulation thickness.
- The diluent air, quencher and heat exchanger concepts are approximately the same in cost (within the error of the cost analysis). As such, other criteria (e.g., system safety, operability, etc.) should be used for selection of the system.

4.4 Thermal Effects on Cement and Concrete

In order to determine whether or not the hot gas treatment can cause thermal damage, concrete characteristics at elevated temperatures were evaluated from literature data. The results indicate that many factors influence the high temperature properties of concrete including:

- Type of concrete (e.g. type of aggregate, type of cement, water-cement ratio, aggregate-cement ratio, curing conditions)
- Whether the concrete is restrained during heating
- Whether the concrete is subjected to thermal cycling
- Whether the concrete is tested while hot or after cooling
- Whether the concrete is quenched or allowed to cool slowly
- Length of temperature exposure.
- Highest temperature attained.

The key concrete properties reviewed include compressive strength, flexural strength, modulus of elasticity and thermal expansion. Each of these factors should be considered when evaluating the effect of the hot gas concepts when applied to field concrete structures.

TABLE 38. HOT GAS CONCEPT COST SUMMARY

Flow SCFM	Insul. Inches	Operating Cost ($1000) Building 1	Building 2	Building 3	Total Operating Cost	Total Cost ($1000) Diluent Air	Quencher	Heat Exchanger
1000	2	$ 83.3	$ 96.7	$23.2	$ 203.2	$ 325.2	$ 348.6	$ 357.6
1000	4	98.0	89.9	27.3	215.2	337.2	360.6	369.6
1000	12	208.6	125.3	42.8	376.7	498.7	522.1	531.1
2000	2	72.5	73.9	20.1	166.5	318.9	346.5	366.9
2000	4	90.4	76.4	23.9	190.7	343.1	370.7	391.1
2000	12	202.5	115.6	41.4	359.5	511.9	539.5	559.9
3000	2	70.3	68.5	19.3	158.1	334.5	361.1	401.3
3000	4	88.5	73.3	23.5	185.3	361.7	388.3	428.5
3000	12	200.9	113.7	40.9	355.5	531.9	558.5	598.7
4000	2	69.4	67.5	19.2	156.1	354.5	380.7	442.9
4000	4	87.9	72.9	23.4	184.2	382.6	408.8	471.0
4000	12	200.3	113.5	41.0	354.8	553.2	579.4	641.6

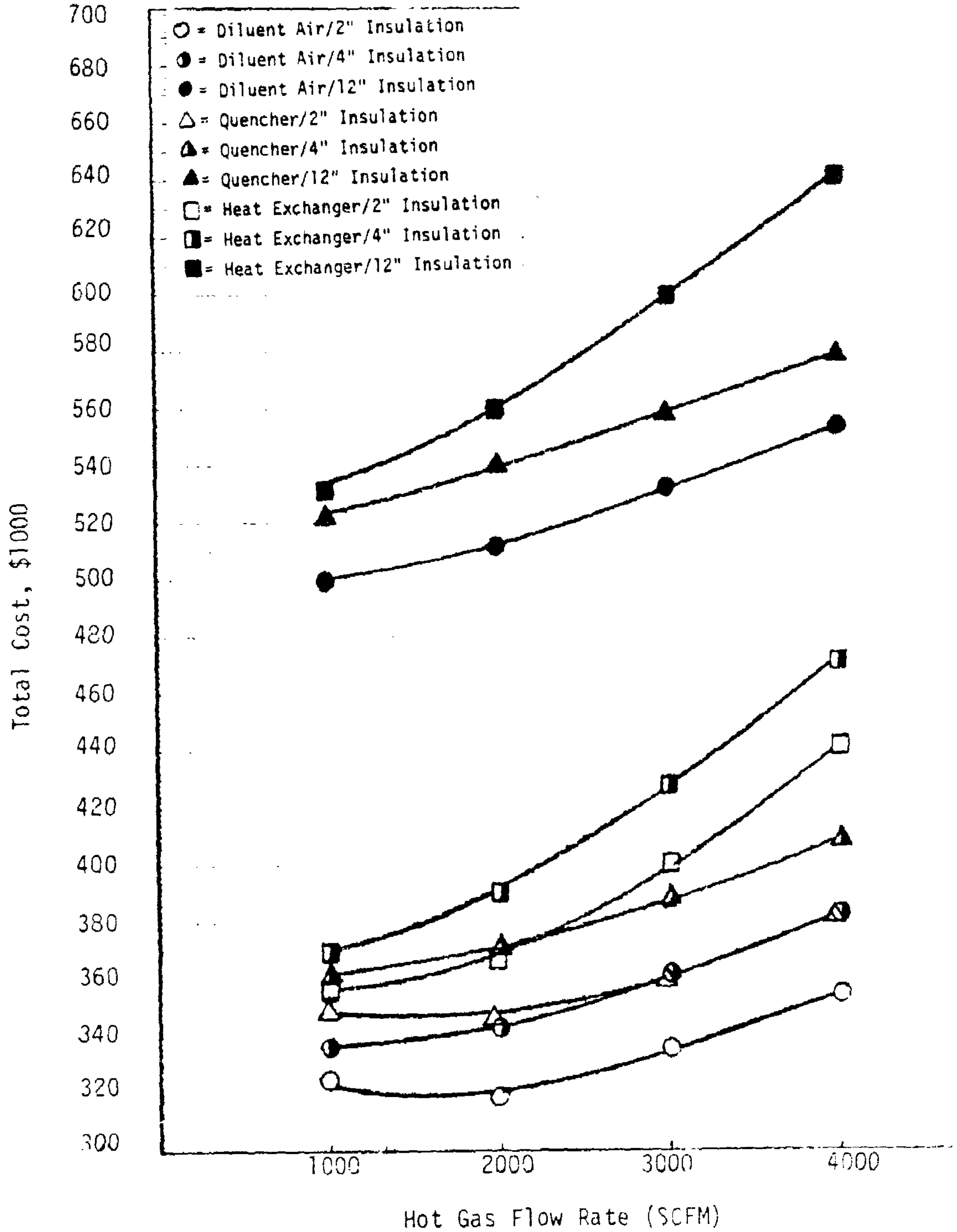


FIGURE 17. SUMMARY OF COSTS FOR APPLICATION OF THE HOT GAS CONCEPT

4.4.1 Thermal Effect on the Compressive Strength of Concrete

Because compressive strength is one of the primary qualities by which concrete is judged, it is probably the most investigated property at high temperatures. Figure 18 shows the data of Abrams[6] for concretes containing carbonate, siliceous and lightweight aggregate, respectively. Carbonate and siliceous aggregates are commonly used in structural concrete while unsanded lightweight concrete is used in the manufacture of masonry block. The testing regime included (1) heating without load and testing while hot, (2) heating at three stress levels and testing while hot, and (3) testing after slowly cooling. The heating time to achieve a uniform temperature was generally 3 to 4 hours. The results can be summarized as follows:

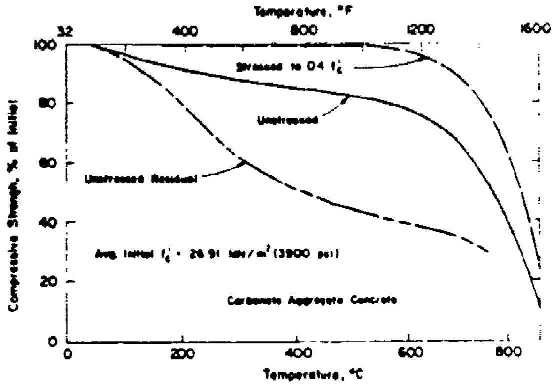
(1) Carbonate and sanded lightweight aggregate concrete retained more than 75 percent of original compressive strength up to 650 C when heated unstressed and tested hot; for siliceous aggregate concrete the corresponding temperature was 430 C.

(2) When loaded during heating, compressive strengths were 5 to 25 percent higher, but were not affected by the applied stress level. The smaller strength loss under stressed condition is attributed to a retardation of crack formation.

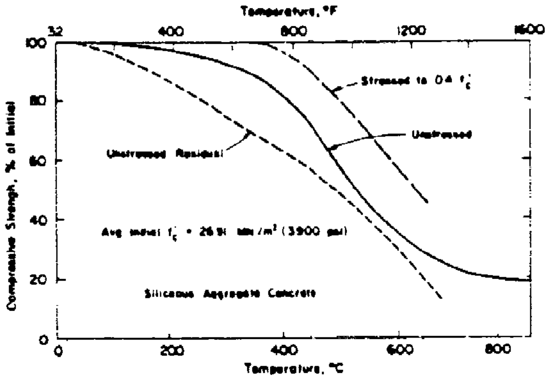
(3) Residual compressive strengths after cooling were significantly lower than the corresponding hot compressive strength for unstressed concrete.

(4) The original strength of the concrete had little effect on the percent reductions in strength observed.

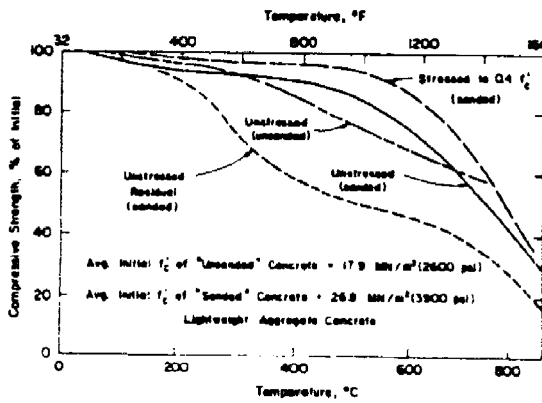
The above observations agree fairly well with other investigations; however, layer reductions in compressive strength have been reported under similar test conditions[7]. In addition, the results of Weigler and Fischer[3] indicated that stressed specimens have a residual strength equal to or greater than companion specimens not stressed during heating (at a test temperature of 450 C).



Compressive strength of carbonate aggregate concrete at high temperature and after cooling



Compressive strength of siliceous aggregate concrete at high temperatures and after cooling

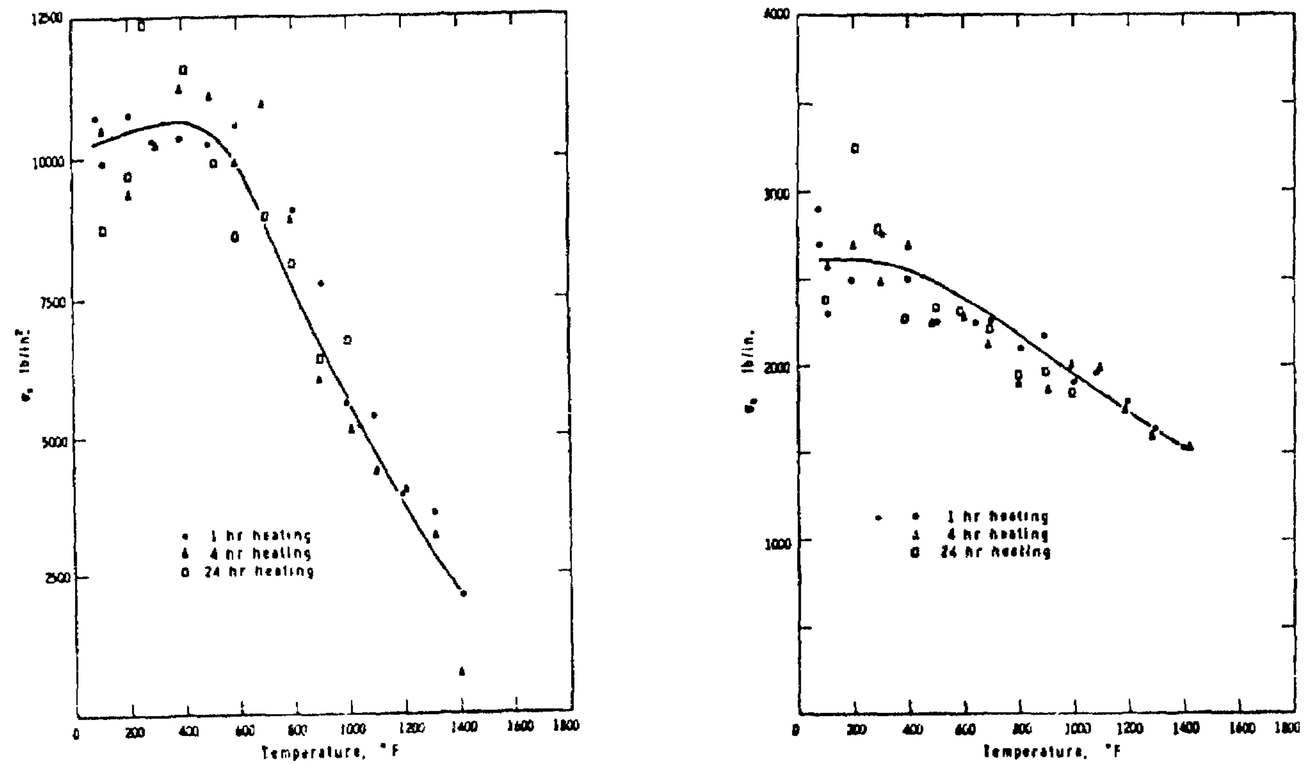


Compressive strength of lightweight concrete at high temperature and after cooling

FIGURE 18. COMPRESSIVE STRENGTH OF CONCRETES AT ELEVATED TEMPERATURES(6)

The amount of residual strength after cooling requires further discussion. Zoldners[9] showed that up to about 500 C, there is a greater reduction in residual compressive strength when concrete is water quenched than when slowly cooled. This was attributed to thermal shock. Little difference in strength at higher temperatures was found between quenched and slowly cooled specimens. In contrast, Crook and Murray[10] found that an increase in residual strength could be obtained by water immersion. In their tests, masonry blocks were maintained at a temperature of 620 C for 20 minutes. The blocks were then re-cured by immersion in water (either for 2 minutes or for 24 hours) and then left to air cure for periods of up to 28 days. It was not stated whether the blocks were first allowed to cool before water immersion. The results indicated that a 24 hour immersion time followed by air curing resulted in complete regain of original compressive strength. Although the time the material was held at 620 C was relatively short, the results demonstrate that a loss of compressive strength can be recovered by proper water treatment.

Figure 19 gives results from Harmathy et al.[11] on compressive strength for Portland cement (no aggregate) and lightweight concrete masonry as a function of three heating times. Testing was performed while the samples were hot. From the results, it appears that heating for short time periods (i.e. less than 24 hours) has little effect on the measured concrete properties at elevated temperatures. The data also show that lightweight masonry block is quite stable at high temperatures (at 538 C, 77 percent of compressive strength remains), whereas Portland cement rapidly loses strength at high temperatures (at 538 C, 8 percent of compressive strength remains). A comparison of Figure 18 with Figure 19 indicates that the loss of compressive strength at high temperatures is much greater for the Portland cement without added aggregate. This suggests that the aggregate stabilizes concrete at high temperatures. The stabilizing effect of aggregate is supported by the data by Malhotra[3], who found that above 204 C, lean mixes (high aggregate contact) showed a proportionally smaller reduction in compressive strength than occurred with richer mixes.



Ultimate strength in compression of hydrated portland cement (w_o/c = 0.33) at elevated temperatures

Ultimate strength in compression of a lightweight concrete of expanded shale aggregate at elevated temperatures

FIGURE 19. ULTIMATE STRENGTH OF CONCRETES AT ELEVATED TEMPERATURES(10)

(Copyright permission received from the American Concrete Institute)

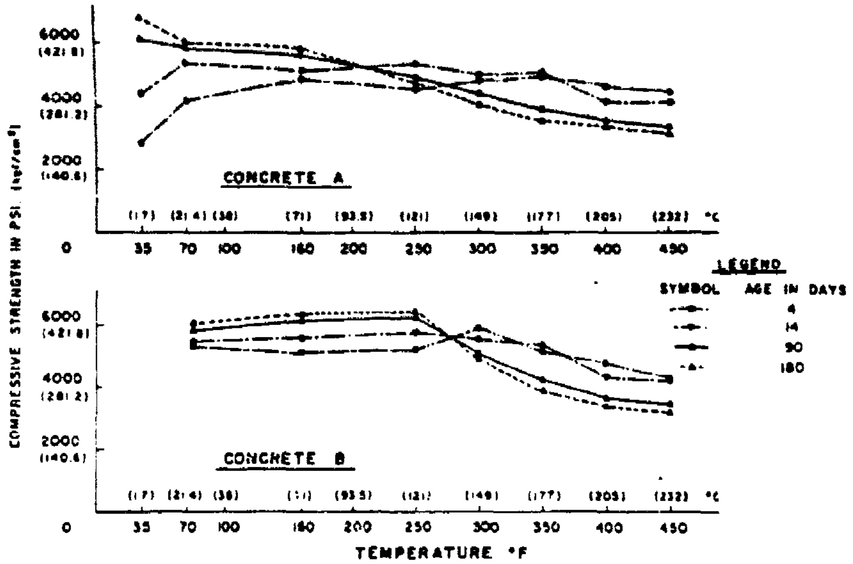
Figure 20 shows the effect of temperature on compressive strength of dolomite/hornblende aggregate concrete at prolonged heating times.[12] The concrete specimens were sealed during the thermal treatment to prevent moisture loss and were allowed to cool slowly before testing. Concrete A had a 1 day cure before heating, and concrete B had a 14 day cure before heating. Above 150 C, the compressive strength gradually decreases as the heating time increases. At 230 C, about 75 percent of the initial compressive strength remains after 14 days. It should be pointed out that moisture loss was prevented during heating by a saturated steam environment which surrounded the specimen. This may have caused a more adverse effect on the concrete properties than when the moisture is free to evaporate.

4.4.2 Thermal Effect on the Modulus of Elasticity of Concrete

In general, the modulus of elasticity of concrete at high temperatures follows the same trends as compressive strength.

4.4.3 Thermal Effect on the Flexural Strength of Concrete

Zoldners[9] tested the flexural strength of several types of concrete up to 700 C. The samples were heat treated at the test temperature for one hour and then allowed to slowly cool to room temperature. Figure 21 shows the flexural strength as a function of temperature. The results are somewhat dependent on the type of aggregate, but generally a significant decrease in the flexural strength occurs at relatively low temperatures. At 300 C, approximately 50 percent of the flexural strength remains. Thus, at elevated temperatures, flexural strength decreases to a greater extent than compressive strength. However, the flexural strength of concrete is generally not as significant a parameter as compressive strength in relation to the structural integrity of a building.



Compressive strength versus temperature for both Concretes A and B at indicated ages

FIGURE 20. COMPRESSIVE STRENGTH OF CONCRETE HELD AT ELEVATED TEMPERATURE FOR PROLONGED PERIODS(12)

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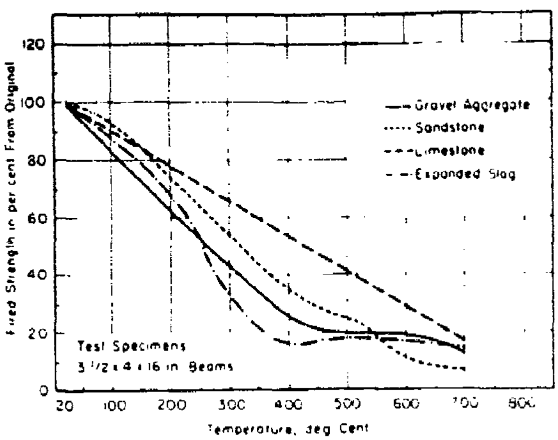


Loss of Flexural Strength

FIGURE 21. FLEXURAL STRENGTH OF CONCRETE AT ELEVATED TEMPERATURES(9)

(Copyright permission received from the American Society for Testing Materials)

4.4.4 Effect of Thermal Cycling on Concrete

The effect of thermal cycling on concrete strength is another important consideration. Campbell-Allen et al[14,15] tested compressive strengths of several types of aggregate concrete up to 300 C and noted a progressive deterioration with increasing numbers of thermal cycles, although most of the loss occurred in the first few cycles.

Livovich[16] conducted cyclic heating tests at 425, 538, and 650 C on several types of cement containing crushed fire brick aggregate. The cyclic heat tests consisted of firing specimens for 16 hours at a given temperature and then cooling for 8 hours in air until ten such cycles were completed, or until failure (crumbling) of the specimens occurred. At 425 C, the lowest temperature tested, specimens made with Portland cement were severely cracked at the end of ten cycles. However, by placing the concrete in a desiccator during cooling, it was found that after 10 cycles at 538 C, no sign of distress could be detected. This indicates that the main cause of cracking and failure in cyclic heating is the rehydration and subsequent expansion of the dehydrated cement. In contrast to the Portland cement specimens, calcium aluminate cements (used in refractory concrete) are quite stable to cyclic heat, even at 650 C.

4.4.5 Thermal Expansion of Concrete

The thermal expansion of concrete at elevated temperatures results from complex physical and chemical changes involving the cement paste and aggregate. These changes include true thermal expansion (based on kinetic molecular movements) of both cement and aggregate. Volume changes are a result of dehydration reactions and changes in physical form of the component materials (e.g. phase changes in quartz-crystals). Many factors affect the magnitude of the overall thermal volume change including initial moisture control, mineral composition and structure of the aggregate, aggregate to cement ratio, age of concrete, rate and duration of heating, and load level.

After a slight initial expansion at temperatures up to 100 C, a shrinkage of the cement paste occurs as dehydration takes place. This shrinkage is counteracted by expansion of the aggregate.The resultant effect is a sum of the volume changes of cement paste and aggregate at the temperature of exposure. After dehydration is complete, the cement paste will again expand, although expansion may not compensate for the initial shrinkage.

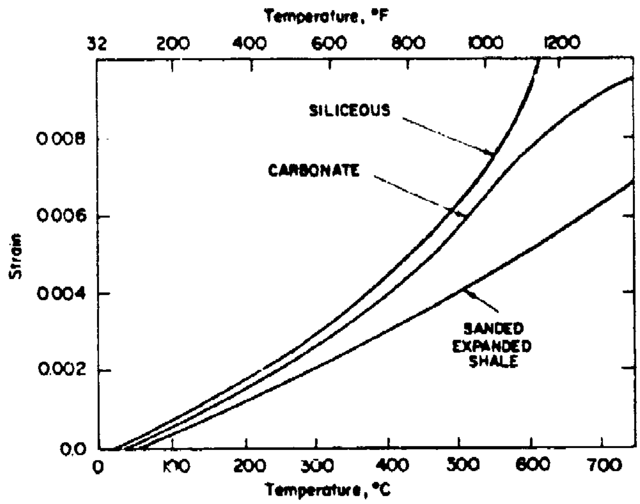
Figure 22 illustrates expansion data of concrete made with several types of aggregate as a function of temperature under conditions of zero applied stress.(6,9) In Figure 22a, the strain is measured at the test temperature, while in Figure 22b, the strain is measured after cooling from the test temperature. At all temperatures, a net expansion results when the strain is measured at the test temperature (Figure 22a). However, up to about 300 C the strain is recoverable upon cooling (i.e., no permanent dilution) as shown in Figure 22b.

When a load is applied to concrete during heating, a pronounced effect on thermal expansion results. Thermal expansion is strongly reduced as the stress level is increased, and above about 40 percent of the ultimate stress, a net shrinkage occurs at all temperatures(17). This reduction in thermal expansion is attributed to plasticity of the cement paste at elevated temperatures.

The stresses from thermal loadings caused by overall expansion or contraction, when coupled to those arising from mechanical loadings, determine the imposed total stress levels in the concrete. Because of complex stress-strain interactions at elevated temperatures, it is difficult to predict the performance of concrete unless specifications of concrete type and loading conditions are made. However, because of the plasticity of the cement at elevated temperatures, and the fact that below 300 C most strain is recoverable upon cooling, minimal stress damage is likely at temperatures below 300 C.

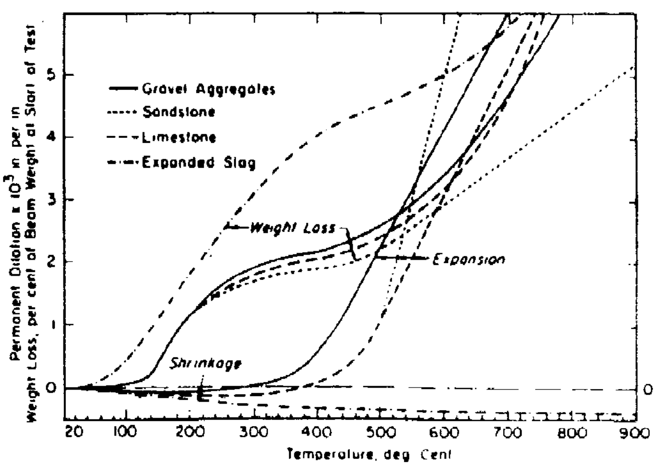
4.4.6 Thermal Cracking of Concrete

Differential strains and stresses between the cement and aggregate in concrete at elevated temperatures can give rise to



Thermal expansion of concrete

Figure 22a.



Expansion and Weight Loss of Concretes

Figure 22b.

FIGURE 22. THERMAL EXPANSION OF CONCRETES AT ELEVATED TEMPERATURES

cracking. Thermal cracking may range from cracking on the surface and microcracking to deeper and substantial cracking of structural significance at locations where overall structural deformations exceed the tensile capacity of the concrete. Concrete spalling can also occur if the moisture content is particularly high.

Table 39 presents some qualitative observations regarding cracking of several types of heat exposed concrete.(9) For most concretes, temperatures below 400 C can be sustained without excessive crack damage.

4.4.7 Conclusions of the Literature Review on the Thermal Effects on Concrete

A review of the literature suggests that in order to minimize structural damage the concrete structures should not be exposed to a temperature greater than about 400 C (752 F). Also, wetting the concrete with water following cool-down after the hot gas treatment is recommended such that the concrete strength can be regained.

4.5 Hot Gas Decontamination Recommendations/Conclusions

Results of the engineering analysis indicate that application of the hot gas decontamination concept to decontaminate field structures contaminated with agent GB, VX or HD is feasible. A summary of recommended features for a hot gas decontamination process is given in Table 40. A piping and instrumentation diagram is given in Figure 23 while an artist's conceptualization is shown in Figure 24.

TABLE 39. PHYSICAL PROPERTIES OF CONCRETE EXPOSED TO ELEVATED TEMPERATURES[9]

(Copyright permission received from the American Society for Testing and Materials)

Aggregate	Temperature, deg Cent	Aggregate-Mortar Bond	Ruptured Surface	Conclusions
Gravel	200 to 400	Strong; few boundary cracks	2 to 5 percent across small[a] aggregate particles, least at 400 C.	Start of bond yield at 400 C; some aggregate may be expanding.
	500, 600	Weakened; yielding along aggregate surfaces; fine mortar cracks.	1 to 2 percent across particles less than 3/8 in.; quench 600 C;	Cement decomposes; some aggregate particles expanding.
	700, 800	Poor; aggregate particles loose, concrete exfoliating.	1 to 2 percent across friable particles; powdery cement; micaceous particle pop-outs.	Mortar bond destroyed by beat; pop-outs from expanding particles.
Limestone	200 to 400	Strong; few boundary cracks.	5 to 10 percent across small[a] aggregate.	Heating: no visible effect.
	500, 600	Weakened; yielding along aggregate surfaces; fine mortar cracks.	5 percent across small[a] aggregate at 500 C; less than 1 percent at 600 C quenched.	Heating decomposes cement; quench: fine cracks at 600 C.
	700, 800	Weak; abundant cracks; powdery cement; limestone decomposing.	1 to 5 percent across small[a] aggregate. Cylinder expanding, cracking on outside.	Heating decomposed cement; limestone starting to decompose at 700 C.
Sandstone	150 to 500	Strong; quenching at 500 C yields fine mortar cracks.	5 percent across small[a] aggregate.	Heating: no visible effect; quench: fine cracks at 500 C.
	600, 700, 800	Weakened; aggregate clean on surface; fine mortar cracks.	2 to 5 percent across weaker particles. 700 C; expanded, cracked cylinders.	Heating breaks down cement. Note: quartz $\alpha \rightarrow \beta$ at 573 C weakens.
Expanded slag	200 to 600	Strong: contact cracks, clean surfaces at 600 C (weakened).	15 to 20 percent across small[a] aggregate. Follows large aggregate surfaces.	Heating: no visible effect; quench: fine cracks at 600 C.
	700, 800	Weakened, cracking along grain boundaries.	5 percent across small[a] aggregate. Inter-aggregate cracks, powdery cement.	Heating decomposes cement.

(a) Note - "Small" aggregate refers to particles 1/4 to 1/2 in. in diameter.

TABLE 40. RECOMMENDED FEATURES FOR A HOT GAS DECONTAMINATION PROCESS

Process Feature	Criteria for Recommendation
7mm Btu/hr hot gas supply system	• Provides a range of hot gas flow rates and temperatures (i.e., 1000 to 2000 scfm, 1500 to 2000 F) which allow decontamination of buildings representative of field structures. • Burner turn-down (i.e., reduction of hot gas flow rate/temperature) may be employed to prevent overheating of concrete. • Economically preferred over systems with higher heat duties. • Off-the-shelf equipment available.
Afterburner for treatment of building exhaust gas	• Destroy traces of agent that volatilize from the building during the decontamination process. • Demonstrated technology. • Off-the-shelf equipment available.
Quencher to cool afterburner exhaust gas	• Cooling of afterburner exhaust gas required in order to use induced draft fan • Comparable in cost to heat exchanger cooling and diluent air cooling. • Provides high humidity in gas stream which favors hydrolyses of any remaining agent. • Off-the-shelf equipment available. • Demonstrated technology.
Induced draft fan	• Maintain the building under a slight negative pressure to prevent release of agent vapors. • Off-the-shelf equipment available.
Insulation equivalent to R = 40	• Allows external building surfaces to reach a temperature of 300 F. • Economically favored over higher R values.

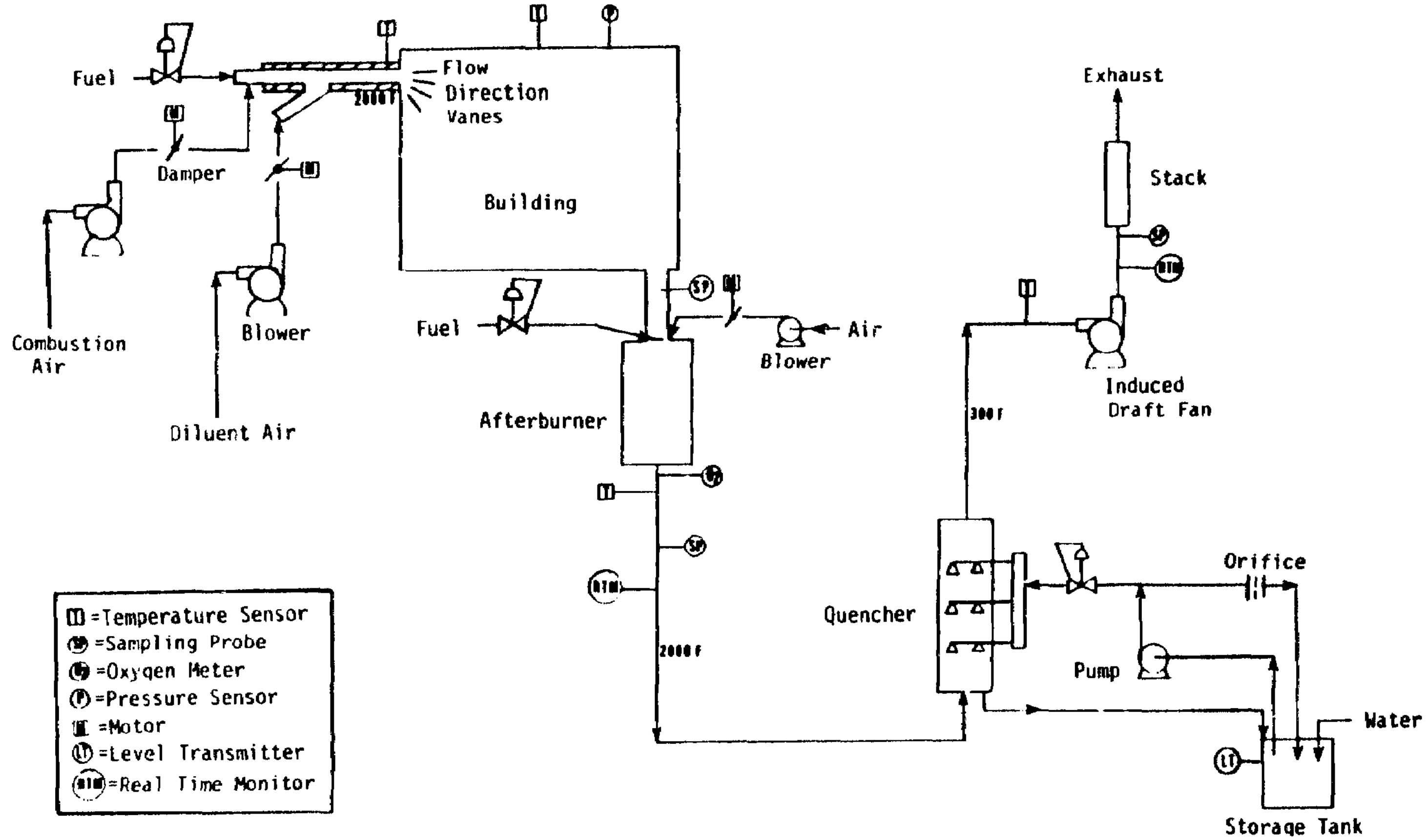


FIGURE 23. PRELIMINARY P & I DIAGRAM OF THE HOT GAS CONCEPT

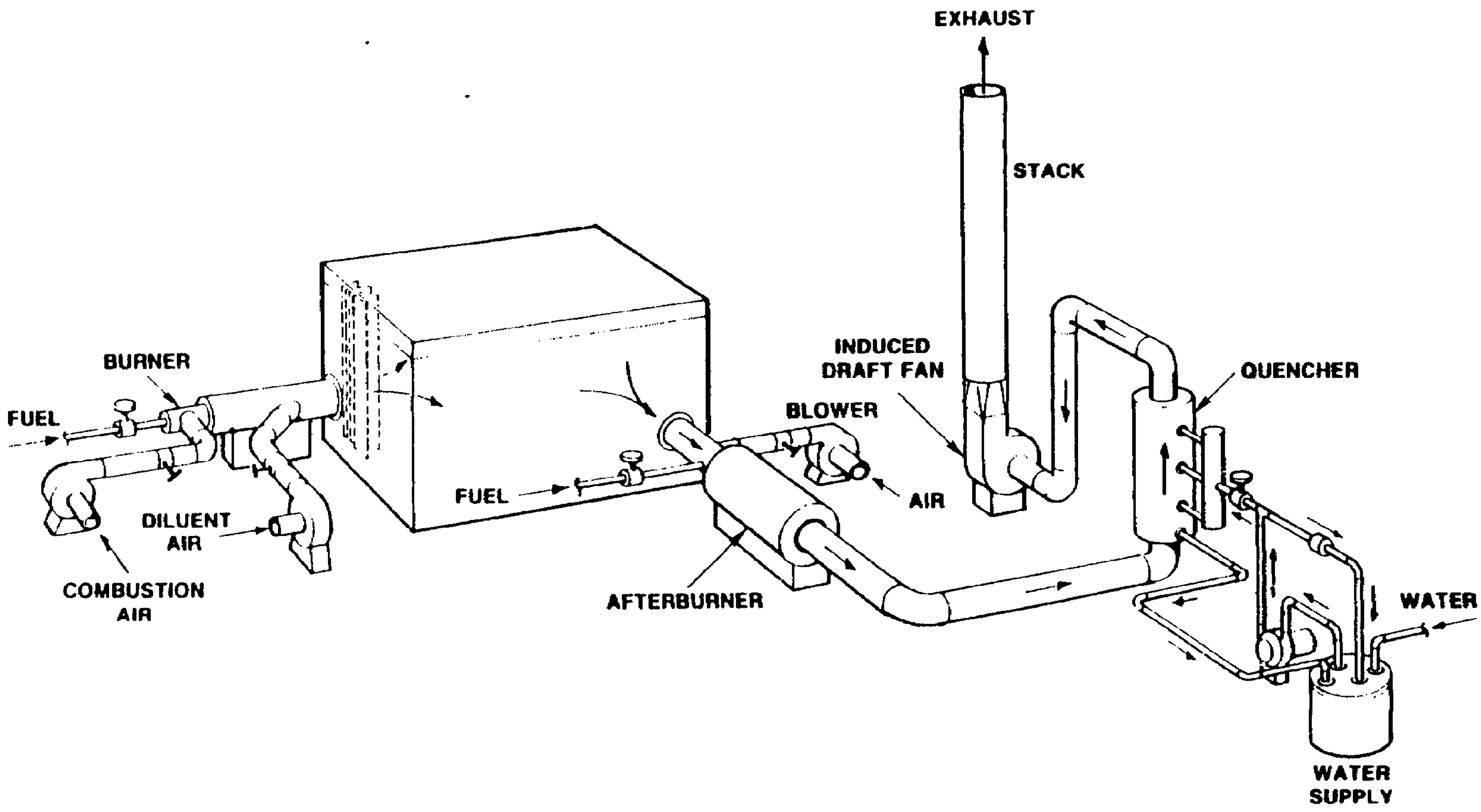


FIGURE 24. CONCEPTUALIZATION OF THE HOT GAS DECONTAMINATION CONCEPT

5.0 STEAM DECONTAMINATION CONCEPT

The steam decontamination concept involves the use of steam to decontaminate materials such as steels and concrete by hydrolysis and/or physical removal (i.e. volatilization and solubilization) of trace quantities of agent. The conditions for decontamination and constraints in the process that were determined through experimental evaluations in Subtasks 5[3] and 6[4] are as follows.

- Painted and unpainted mild and stainless steels contaminated with HD, GB, or VX can be decontaminated to below the detectable limit by maintaining the surface at a temperature near the boiling point of water for 60, 60, or 240 minutes, respectively.
- Steam decontamination includes the physical removal of undecomposed agent by volatilization and wash-off. Thus, a method to remove/decompose agent contained in the exhausted steam and condensate obtained from the building must be incorporated into the overall decontamination process. Experimental results[3] indicate that re-boiling condensate contaminated with agent will cause decontamination.
- Concrete contaminated with HD and porous materials (e.g., unglazed porcelain) contaminated with GB and VX can be decontaminated to below the detectable limit by maintaining the material at a temperature near the boiling point of water for 60, 60, and 240 minutes, respectively.
- Agent may diffuse through porous materials from regions of high temperatures to regions of lower temperatures.

These process conditions/constraints were used to perform heat balances and to specify and cost the decontamination equipment.

5.1 Building Heat Transfer Calculations

Heat balances were performed on each of the three representative agent-contaminated structures described in Table 1. In the heat balances, the steam flow rate, degree of superheat (i.e. inlet steam

temperature) and insulation thickness were varied to evaluate their effect on the feasibility and cost of the concept. The range of values used for the variables are as follows.

- Steam flow rate - 5000, 10,000 and 15,000 lb/hr
- Inlet steam temperature - 300, 400 and 600 F
- Insulation thickness - 2, 4 and 12 inches*

A description of the calculation procedure and the results of the calculation are given in the next sections. In addition to the heat balances, unsteady state mass transfer calculations were performed to determine the rate of diffusion of steam into porous materials such as concrete.

5.1.1 Steam Heat Transfer Calculation Procedure

The method used to calculate heat requirements and times for each of the buildings involved an iterative method similar to the one used for the hot gas concept (see Section 4.1.1). The following modifications to the calculation procedure were made for adaption to the steam process.

- Physical properties of steam rather than physical properties of air were used
- Heat transfer from the steam to the building during the initial stage of the process is by condensation. After the outlet temperature exceeds 212 F, heat transfer is by conduction, radiation, and convection from the gas phase
- Film condensation was assumed for calculation of the inside heat transfer coefficient during the condensation stage.

5.1.2 Results of Steam Heat Transfer Calculations

The results of the steam heat transfer calculations for the three buildings are given in Tables 41 through 43.

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* An insulation thickness of 0 inches was evaluated but did not allow the requirement of heating all building materials throughout to a temperature of about 212 F.

TABLE 41. RESULTS OF STEAM DECONTAMINATION HEAT BALANCES FOR BUILDING 1[a]

Steam Flow Rate, lb/hr	Inlet Steam Temperature,[b] F	Insulation Thickness,[c] Inches	Time to Reach Temperature,[d] Hours	Boiler Duty, MM Btu/hr	CH_4 Required[e] 1000 scf
5,000	400	2	>300	6.15	-
		4	>300		-
		12	>300		-
	600	2	>300	6.62	-
		4	183		1214
		12	140		929
10,000	400	2	>300	12.31	-
		4	251		3096
		12	175		2159
	600	2	99	13.25	1314
		4	82		1089
		12	74		982
15,000	300	2	>300	17.76	-
		4	>300		-
		12	>300		-
	400	2	226	18.46	4180
		4	147		2719
		12	119		2201
	600	2	66	19.87	1314
		4	59		1115
		12	55		1095

a) Building 1 is modeled after Building 412 of Rocky Mt. Arsenal. It is 150 feet long by 70 feet wide by 15 feet high concrete (one foot thick) basement with wood superstructure. It is assumed the wood structure is removed and incinerated leaving a concrete-lined basement requiring decontamination.

b) Inlet is superheated steam.

c) Girders and steel plates are placed over the basement to contain the hot gas. Insulation is then placed on the steel plates to reduce heat losses.

d) Time required for the outside wall temperature to reach 212 F.

e) Natural gas was assumed to be the fuel source.

TABLE 42. RESULTS OF STEAM DECONTAMINATION HEAT BALANCES FOR BUILDING 2[a]

Steam Flow Rate, lb/hr	Inlet Steam Temperature,[b] F	Insulation Thickness,[c] Inches	Time to Reach Temperature,[d] Hours	Boiler Duty, MM Btu/hr	CH_4 Required[e] 1000 scf
5,000	400	2	> 300	6.15	-
		4	> 300		-
		12	254		1565
	600	2	> 300	6.62	-
		4	212		1406
		12	145		962
10,000	400	2	> 300	12.31	-
		4	> 300		-
		12	181		2233
	600	2	243	13.25	3226
		4	141		1872
		12	108		1434
15,000	400	2	> 300	18.46	-
		4	300		5549
		12	157		2904
	600	2	185	19.87	3683
		4	118		2349
		12	94		1872

a) Building 2 is modeled after Building 1501 of Rocky Mt. Arsenal. It has three stories, each 80 feet long by 40 feet wide by 20 feet high. The walls are 2-ft thick reinforced concrete and the floors and ceiling are 1-ft thick concrete.

b) Inlet gas is superheated steam.

c) Insulation is used to reduce heat losses through the concrete walls/ceiling.

d) Time required for the outside wall temperature of the concrete on the first floor to reach 212 F.

e) Natural gas was assumed to be the fuel source.

TABLE 43. RESULTS OF STEAM DECONTAMINATION HEAT BALANCES FOR BUILDING 3(a)

Steam Flow Rate, lb/hr	Inlet Steam Temperature,(b) F	Insulation Thickness,(c) Inches	Time to Reach Temperature,(d) Hours	Boiler Duty, MM Btu/hr	CH_4 Required(e) 1000 scf
5,000	300	2	> 300	5.92	-
		4	> 300		-
		12	> 300		-
	400	2	> 300	6.15	-
		4	> 300		-
		12	125		770
	600	2	126	6.62	836
		4	69		458
		12	55		365
10,000	300	2	> 300	11.84	-
		4	> 300		-
		12	215		2551
	400	2	307	12.31	3787
		4	100		1233
		12	71		876
	600	2	49	13.25	621
		4	39		494
		12	35		444
15,000	300	2	> 300	17.76	-
		4	> 300		-
		12	147		2616
	400	2	118	18.46	2183
		4	70		1295
		12	56		1036
	600	2	36	19.87	717
		4	31		617
		12	29		577

a) Building 3 is modeled after Building 1640 of Rocky Mt. Arsenal. It is 100 feet long by 50 feet wide by 20 feet high metal wall/ceiling structure with a one-foot concrete floor.

b) Inlet gas is superheated steam.

c) Insulation is used to reduce heat losses through the metal walls/ceiling.

d) Time required for the outside wall temperature of the concrete to reach 212 F.

e) Natural gas was assumed to be the fuel source.

Heating times versus steam flow rate curves for varying steam inlet temperatures and insulation thicknesses are illustrated in Figure 25 (Building 1), Figure 26 (Building 2), and Figure 27 (Building 3).

Fuel requirements versus steam flow rate curves for varying steam inlet temperatures and insulation thicknesses are illustrated in Figure ` (Building 1), Figure 29 (Building 2), and Figure 30 (Build 3).

5.1.3 Steam Mass Transfer Calculations

Experimental results from steam decontamination tests indicate that hydrolysis of the agent is a primary decontamination mechanism. The decontamination conditions of high partial pressure of water vapor and elevated temperatures are conducive to vapor phase hydrolysis. As such, decontamination of porous materials must consider not only the conduction of heat into the porous material, but also the presence of a high partial pressure of water vapor within the porous matrix. Two sources of water vapor within a porous matrix are diffusion and in-situ formation.

The rate of diffusion of water vapor into a porous material such as concrete can be estimated by the semi-infinite solution to the one-dimensional unsteady state diffusion equation. The solution is as follows:

$$\frac{P_t - P_o}{P_1 - P_o} = \operatorname{erfc}\left(y/2\sqrt{D_{EFF}t}\right)$$

where

P_t = partial pressure of water vapor inside the material at time t

P_o = partial pressure of water vapor at time 0

P_1 = partial pressure of water vapor at surface of the material at time t greater than 0

erfc = complimentary error function

y = penetration depth = 30.48 cm for a one-foot thick concrete slab

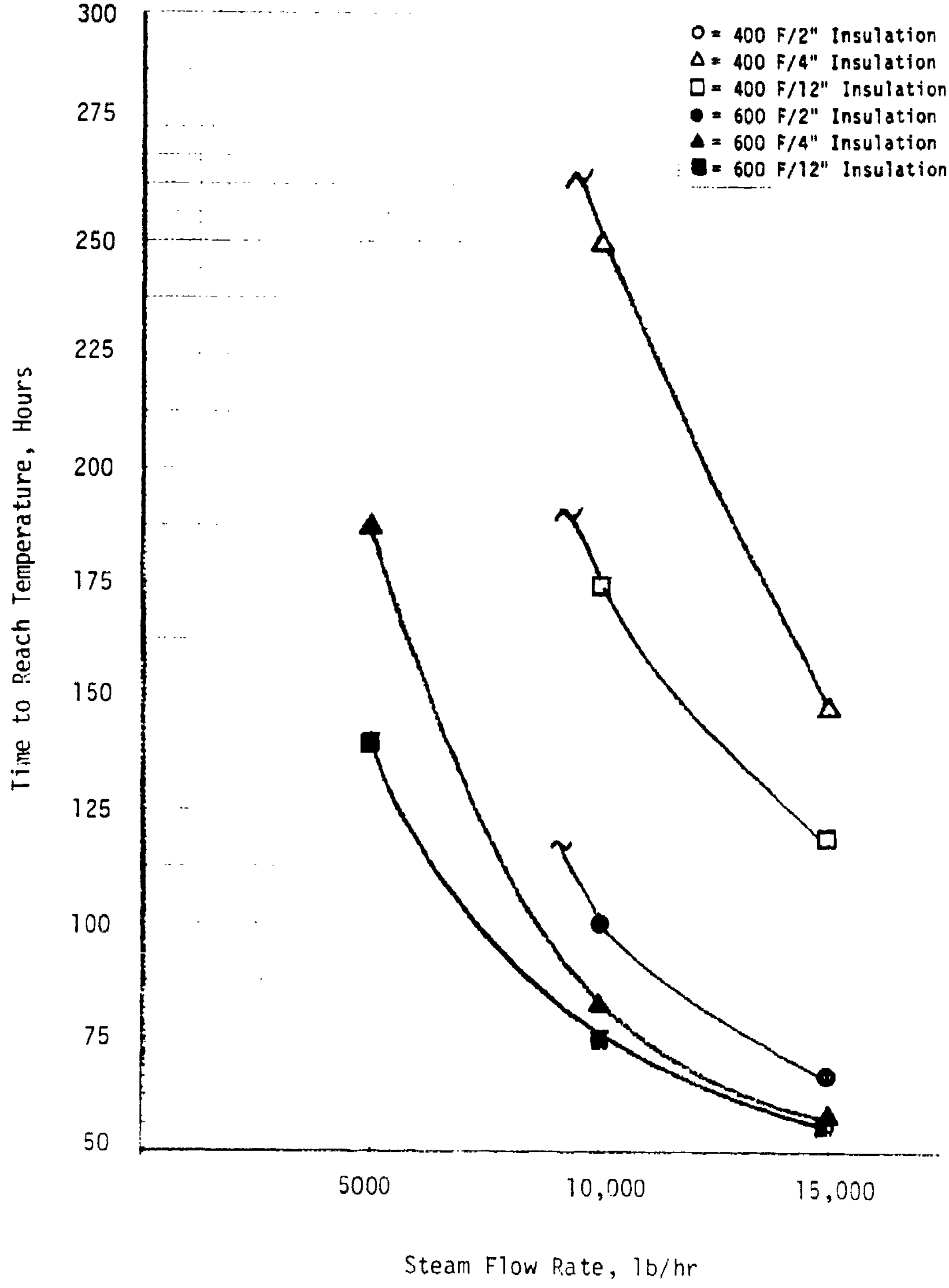

FIGURE 25. HEATING TIMES VERSUS STEAM FLOW RATES FOR BUILDING 1

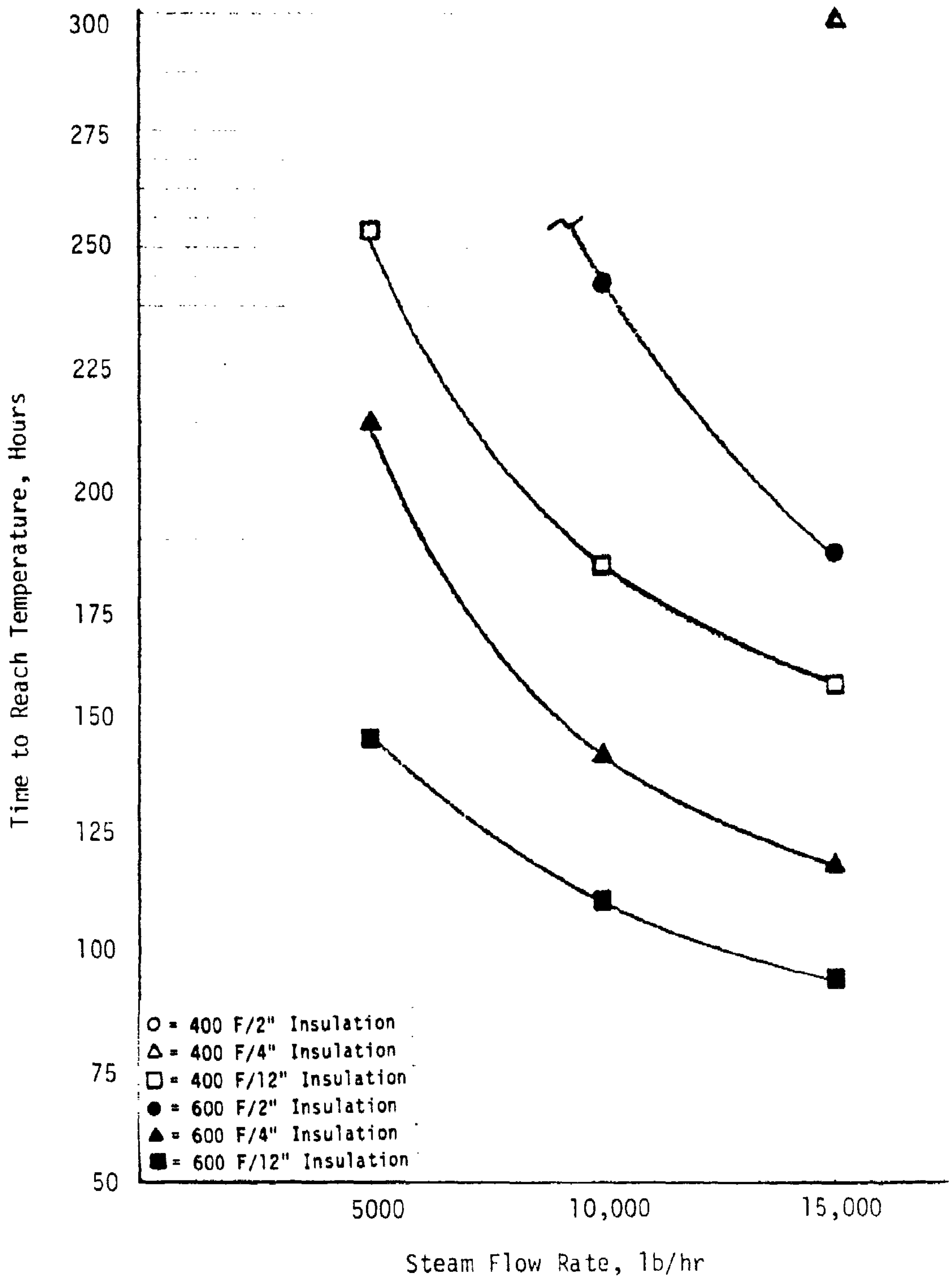

FIGURE 26. HEATING TIMES VERSUS STEAM FLOW RATES FOR BUILDING 2

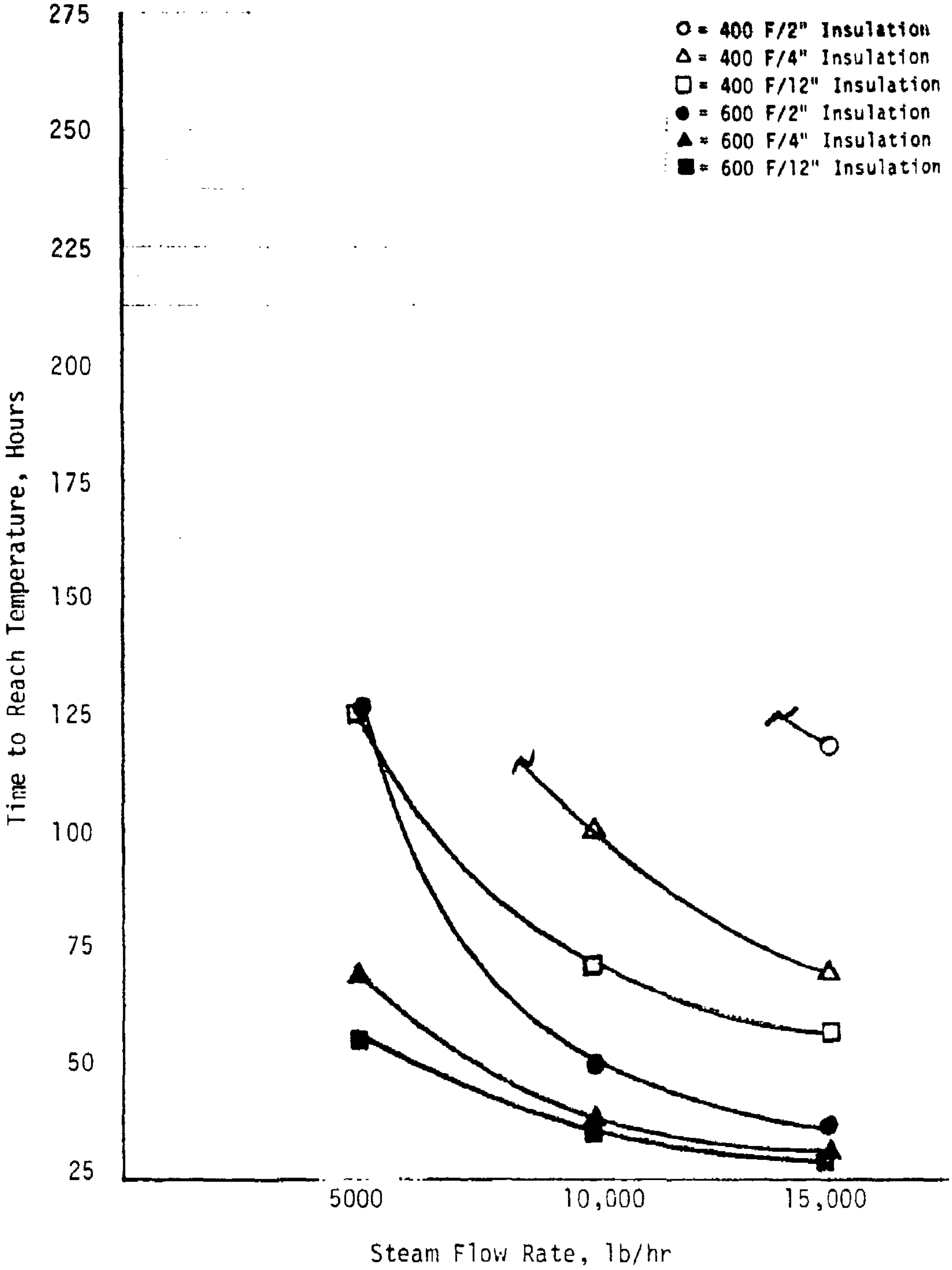

FIGURE 27. HEATING TIMES VERSUS STEAM FLOW RATES FOR BUILDING 3

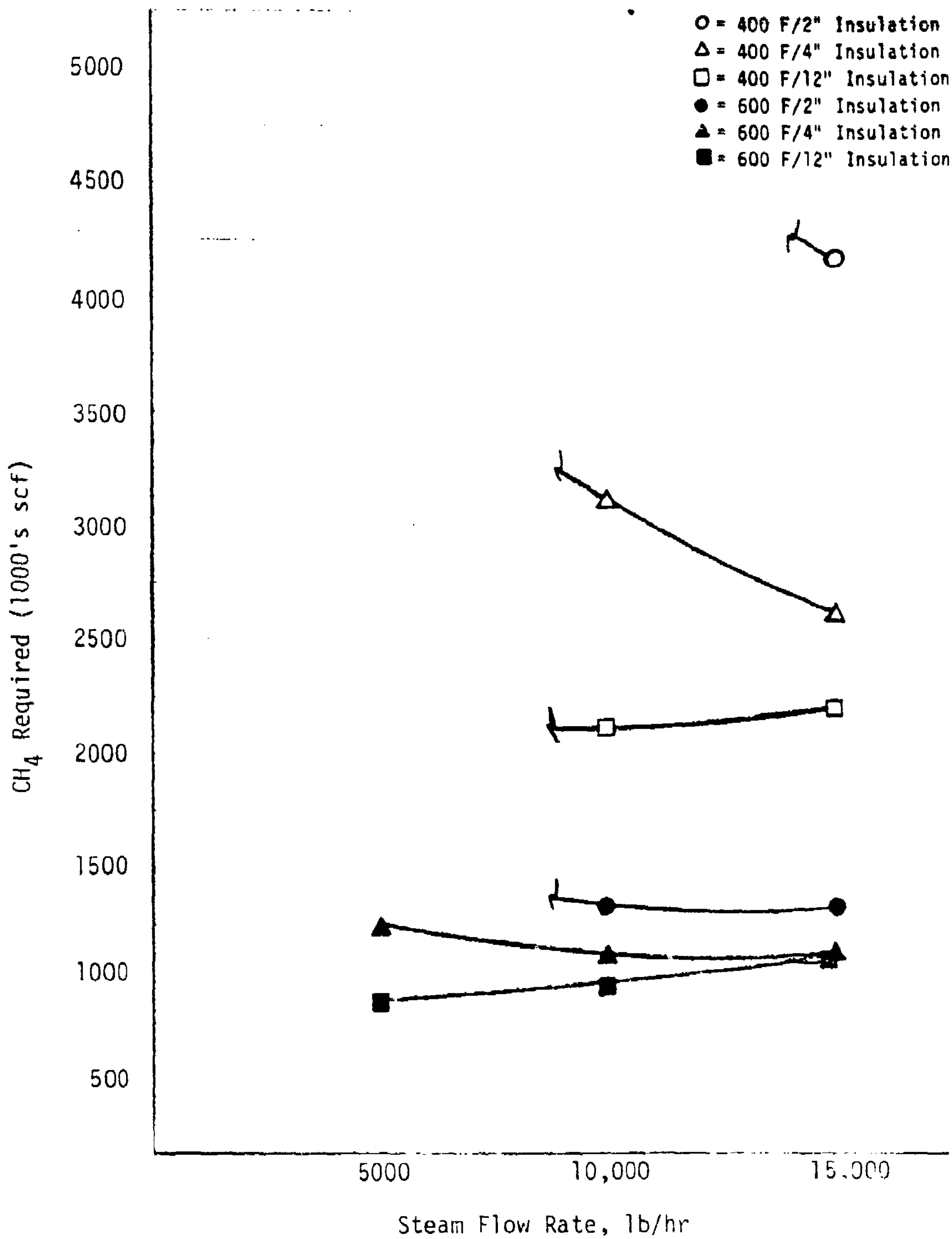

FIGURE 28. FUEL REQUIREMENTS VERSUS STEAM FLOW RATES FOR BUILDING 1

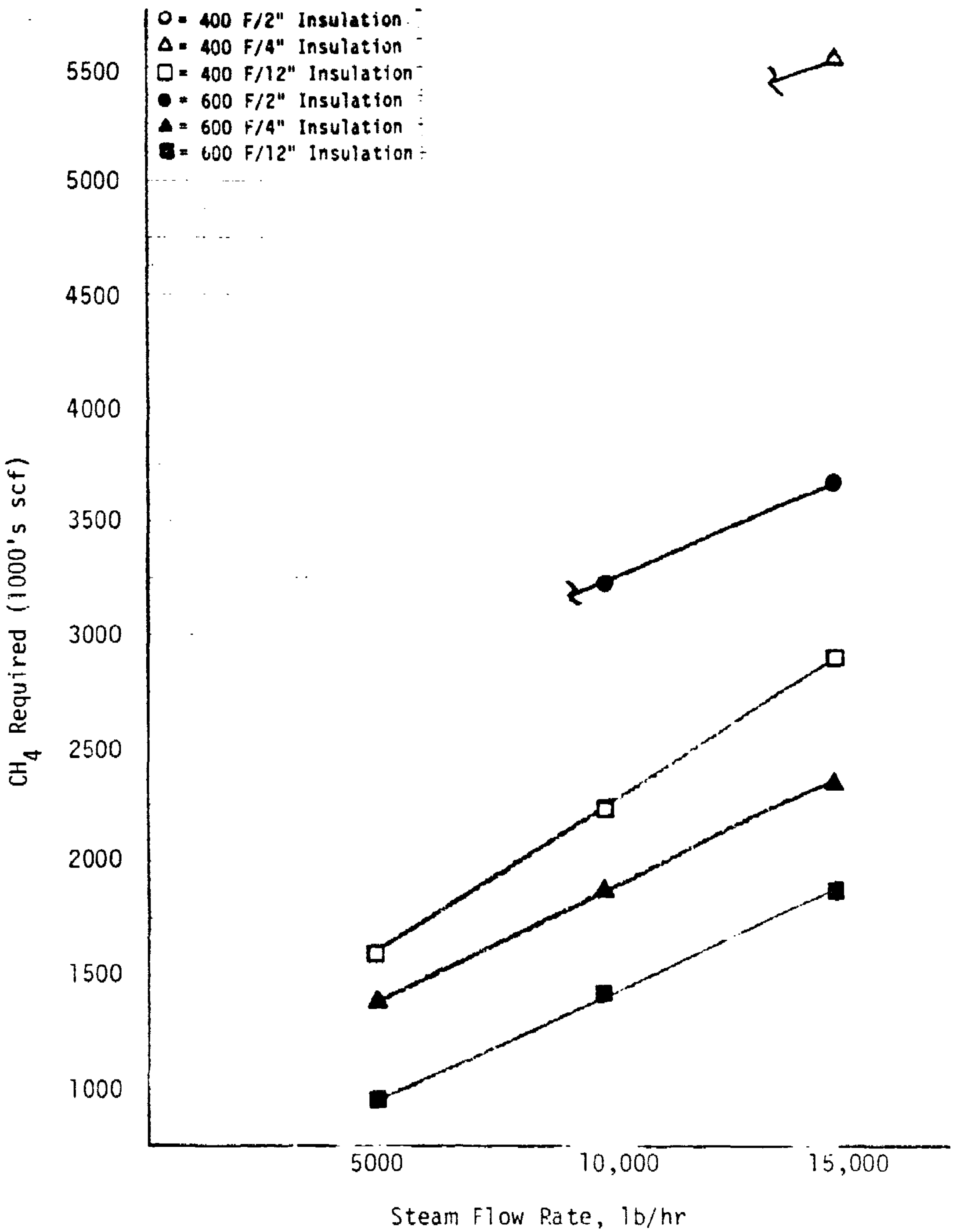

FIGURE 29. FUEL REQUIREMENTS VERSUS STEAM FLOW RATES FOR BUILDING 2

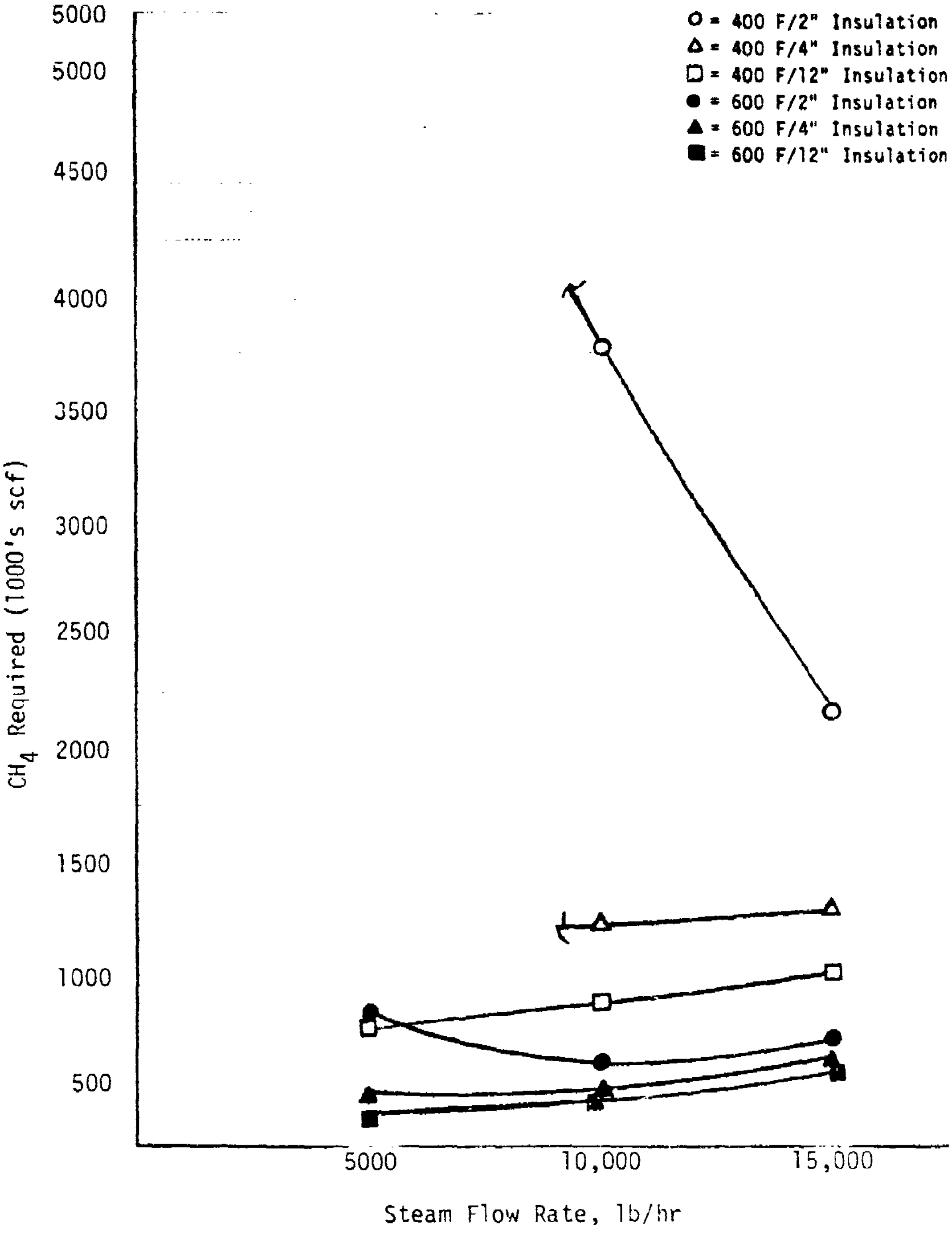

FIGURE 30. FUEL REQUIREMENTS VERSUS STEAM FLOW RATES FOR BUILDING 3

D_{EFF} = effective diffusivity, cm^2/hr

t = time, hr

For 70 F air at 50 percent relative humidity $P_0 = 0.012$ atm. For decontamination using steam at 212 F $P_1 = 1$ atm. The effective diffusivity of steam in air is estimated as follows.

At 100 C, $D_{STEAM/AIR} = 0.34\ cm^2/sec$*

$$D_{EFF} = \frac{D_{STEAM/AIR}\ \epsilon}{\xi} \cong D_{STEAM/AIR}\epsilon^2$$

where

ξ = tortuosity $1/\epsilon$

ϵ = porosity 0.12(2)

$D_{EFF} = 0.34 \times (0.12)^2 \times 3600$ sec/hr

$= 17.63\ cm^2/hr$

The partial pressure of water vapor at a depth of one foot into a concrete slab was calculated with the values above. Results of the calculations, illustrated in Figure 31, indicate that infeasibly long periods of time would be required for the concrete at a depth of one foot or more to reach a high partial pressure of water vapor (i.e. higher than 0.9 atm) by diffusion alone. However, a literature review indicates that when cured concrete is heated to mild temperatures (i.e. up to 980 F), chemically bound and absorbed water evaporates in-situ. The amount of evaporable water in the concrete (5 to 6 weight percent)(18) should be sufficient to achieve the high partial pressure desirable for decontamination. Thus, decontamination of concrete should occur by heat conduction and concomitant in-situ steam generation rather than by a steam diffusional route alone.

5.2 Steam Decontamination Equipment Selection/Costing

Four configurations of the steam decontamination system were evaluated. The four configurations involve different methods to treat uncondensed steam exhausted from the building during the decontamination treatment. The uncondensed steam may contain intact agent. The four configurations, illustrated in Figure 32, are as follows.

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* Estimated with the Chapman-Enskog binary gas pair diffusion equation.

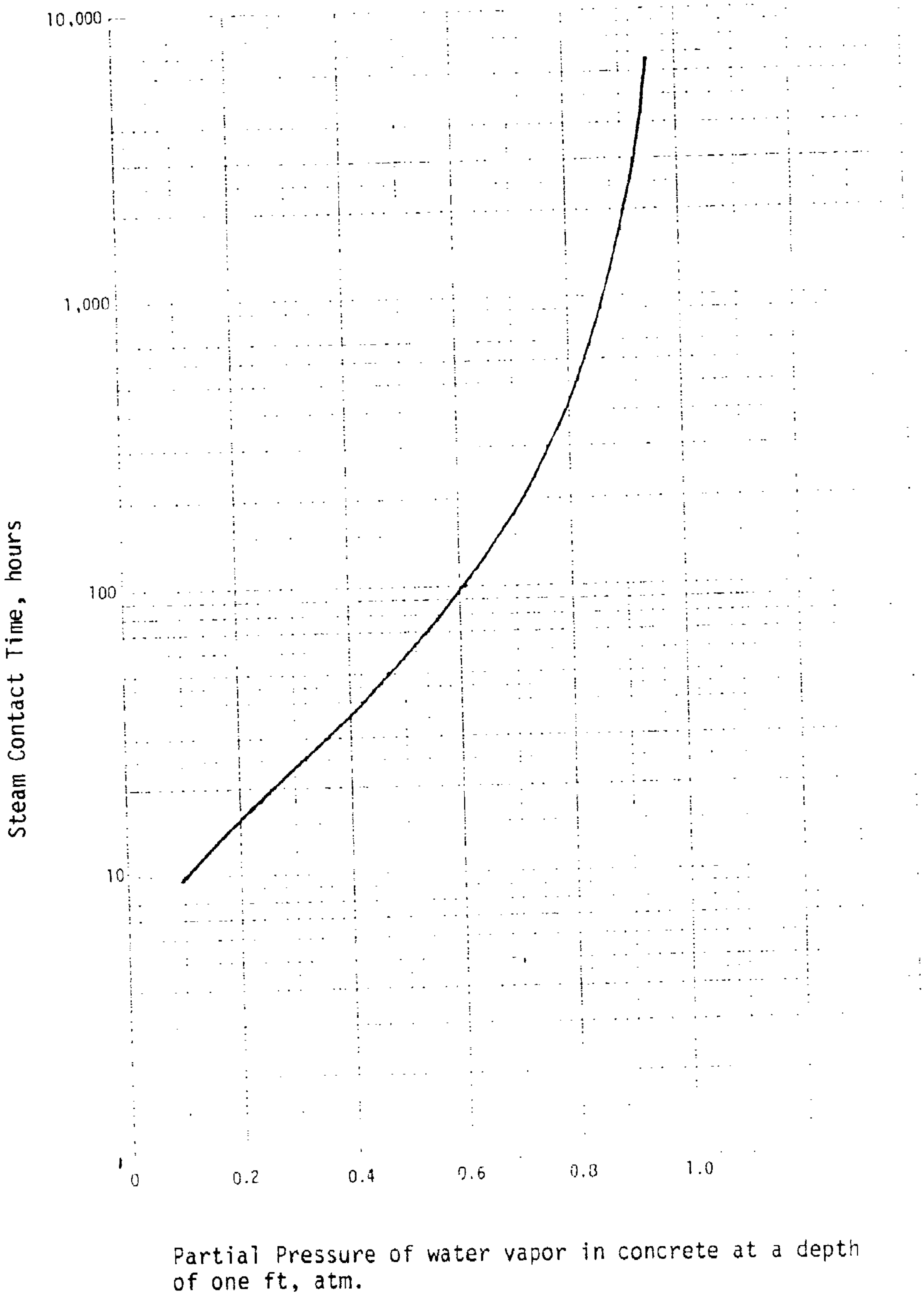

FIGURE 31. DIFFUSION OF WATER VAPOR INTO CONCRETE

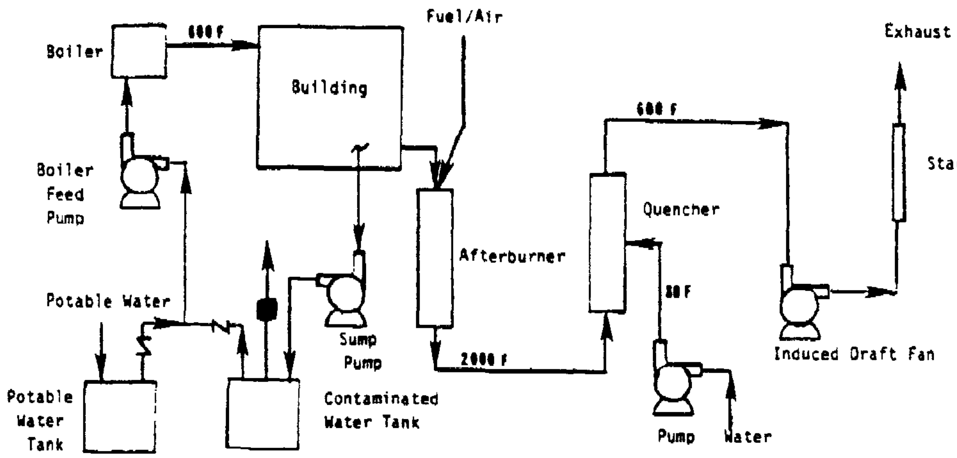

Figure 32a. Afterburner System

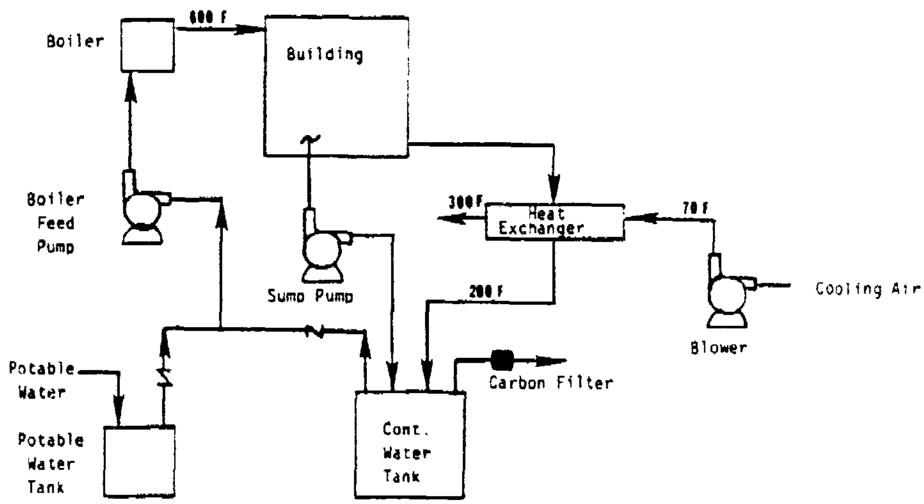

Figure 32b. Heat Exchanger System

FIGURE 32. STEAM DECONTAMINATION EQUIPMENT CONFIGURATION

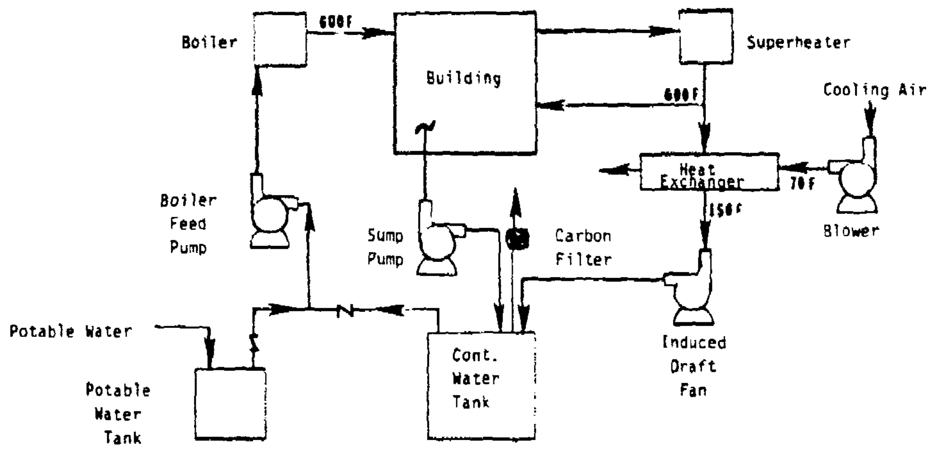

Figure 32c. Partial Recycle System

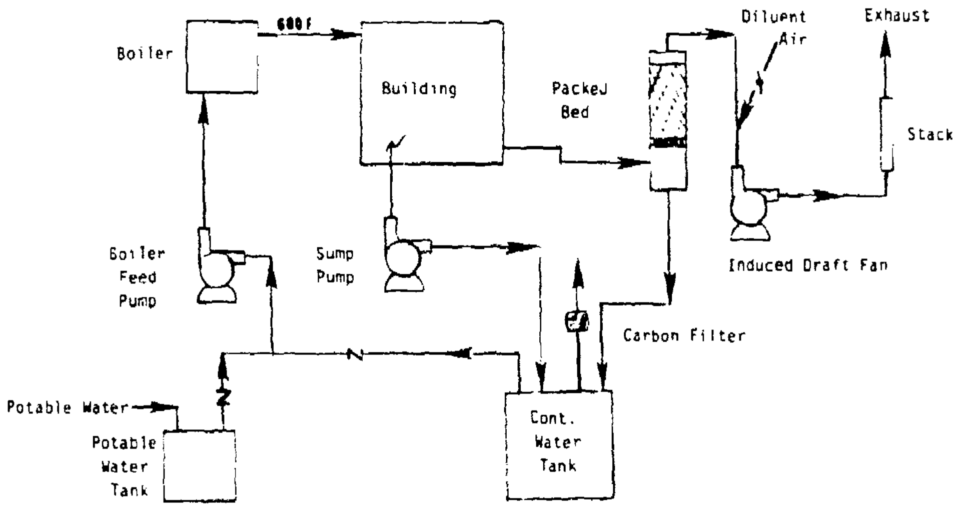

Figure 32d. Packed Bed System

FIGURE 32. (CONTINUED)

- Afterburner thermal treatment
- Heat exchanger condensation followed by recycle to the boiler
- Partial recycle to building (after reheat)/partial condensation by heat exchanger followed by recycle to the boiler
- Packed bed treatment.

In each of the configurations, the condensate from the building is pumped to a storage tank and then recycled to the boiler. Recyling of contaminated water through the boiler should cause decomposition of the trace quantities of agent that may be contained in the water.[4]

A discussion of the four steam decontamination configurations is given as follows.

5.2.1 Steam Decontamination/Afterburner System

The steam decontamination/afterburner system, illustrated in Figure 32a, consists of a packaged boiler (i.e. steam generator), afterburner, quencher, induced draft fan, stack, ductwork, and a condensate collection system. The specification and costing of these items is given as follows.

5.2.1.1 Boiler. The following criteria were used to select a steam generator.

- Indirect fired, fire-tube
- Natural gas or oil fuel capability
- 250 psig steam supply superheated to 632 F in the boiler. The steam is throttled to about 0 psig (600 F) prior to injection into the building
- A packaged unit is preferred. The package should consist of a burner, fans, feed pump, and controls.

A summary of the boiler costs is given in Table 44.

5.2.1.2 Afterburner. A heat balance on the afterburner system gives

$$q_{TOTAL} = q_{AIR} + q_{STEAM} + q_{HEAT\ LOSS}$$

TABLE 44. BOILER SYSTEM COSTS

Steam Flow Rate, lb/hr	Building Inlet Temp., F	Required Heat Duty, MMBTU/hr	Selected Heat Duty,[a] MMBTU/hr	Cost,[b] 1968$	Cost,[c] 1984$
15,000	600	19.9	26.5	$ 40,250	$115,530
10,000	600	13.3	17.7	32,200	92,430
5,000	600	6.6	8.8	20,700	59,420

(a) Normal operation at 75 percent capacity.
(b) Includes preassembled boiler, induced draft fan, instruments, controller, burner, boiler feed pump, stack, combination gas/oil firing. Cost includes 15 percent additional for about a 200 F superheat. (Chemical Engineering 3/24/69, pg. 114).
(c) 1984$ = 1968$ x (783.9/273.1) for 3rd quarter 1984$.

where

$$q_{TOTAL} = 58{,}573\ V_{CH_4}{}^{*}$$

$$q_{AIR} = 2{,}339\ v_{AIR}{}^{*}$$

$$q_{HEAT\ LOSS} = 5{,}857\ v_{CH_4}{}^{*}$$

$$q_{STEAM} = \dot{m}_{STEAM} \times 884.7^{**}$$

$$= v_{STEAM} \times 0.3324$$

Thus, $v_{CH_4} = 0.0444\ v_{AIR} + 0.0056\ v_{STEAM}$.

Allow 5 percent oxygen in the exhaust:

$$0.05 = \frac{0.21\ v_{AIR} - 2v_{CH4}}{v_{CH_4} + v_{AIR} + v_{STEAM}}$$

Combining equations gives

$$v_{AIR} = 0.893\ v_{STEAM}$$

$$v_{CH_4} = 0.045\ v_{STEAM}$$

Results of the heat balance are given in Table 45A. The afterburner chamber is specified in Table 45B. Costs for the afterburner system are given in Table 46.

5.2.1.3 Quencher. Following thermal processing in the incinerator, the hot flue gases will be cooled by quenching to a temperature of about 600 F. A lower quenching temperature was not selected because of the potential for condensation in the gas stream. A quencher rather than the use of diluent air was selected for cooling because of the high flow rates of afterburner flue gas. For example, cooling the afterburner flue gas from the 15,000 lb/hr steam case with air at 70 F would require about 59,000 scfm of air. This yields a combined air flow rate of 137,000 acfm at 600 F which must be handled by an induced draft fan.

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* See Section 4.2.1.2.

** Heat required to raise the steam temperature from 200 F (estimated building exhaust temperature) to 2000 F (afterburner operating temperature).

TABLE 45. AFTERBURNER CALCULATIONS

TABLE 45A. AFTERBURNER MASS BALANCE

Steam Flow Rate, lb/hr	Steam Flow Rate, scfm	v AIR, scfm	v CH_4, scfm	Afterburner Flue Gas (scfm)					% O_2 in Exhaust
				N_2	CO_2	H_2O	O_2	Total	
15,000	4986	4452	224	3517	224	5434	487	9663	5.0
10,000	3324	2968	150	2345	150	3624	323	6442	5.0
5,000	1662	1484	75	1172	75	1812	162	3221	5.0

TABLE 45B. AFTERBURNER CHAMBER SPECIFICATION

Steam Flow Rate, lb/hr	Heat Duty, MMBTU/hr	Minimum Chamber Volume,[a] ft^3	Outside Chamber Diameter,[b] ft	Inside Chamber Diameter, ft	Length, ft	Inside Surface Area, ft^2	Gas Velocity, ft/sec
15,000	13.14	374	6.17	5.5	16	276	31.5
10,000	8.76	249	5.33	4.67	15	220	29.1
5,000	4.38	125	4.00	3.33	14.5	182	28.6

(a) Minimum chamber volume = Total afterburner flue gas (scfm) $\times \frac{2460}{530} \times \frac{1}{60} \times 0.5$ sec.

(b) Includes 4 inches of refractory.

TABLE 46. AFTERBURNER COSTS

Steam Flow Rate, lb/hr	Selected Heat Duty, MMBTU/hr	Burner System Cost,(a) 1984$	Inside Chamber Area, ft^2	Refractory Cost,(b) 1984$	Shell Cost,(c) 1984$	Total Afterburner Cost, 1984$
15,000	14	$10,400	276	$11,320	$20,700	$42,420
10,000	10	9,200	220	9,020	16,500	34,720
5,000	7	7,950	182	7,460	13,650	29,060

(a) See Table 11.
(b) 90 percent alumina firebrick at $\$10.25/ft^2$/inch x 4 inches (Chemical Engineering, 2/6/84, pg. 121).
(c) At $\$75/ft^2$ area (Chemical Engineering, 2/6/84, pg. 121).

A heat balance on the quencher gives:

$$q_{WATER}\Big|_{80\ F}^{600\ F} = q_{GAS}\Big|_{2000\ F}^{600\ F}$$

$$\dot{m}_{WATER} \times (1335.2-48.2) = \dot{m}_{GAS} \times 0.416 \times (2000-600)$$

$$\dot{m}_{WATER} = 0.453\ \dot{m}_{GAS}$$

A summary of quencher calculations and cost estimates is given in Table 47.

5.2.1.4 Induced Draft Fan. An induced fan was selected to maintain the building under a slight negative pressure of about -0.2 inches water. A summary of the induced draft fan specifications and cost is given in Table 48.

5.2.1.5 Ductwork. Ductwork for the system was specified using the criteria given in Section 4.2.4.1.2. The pressure losses obtained from the ductwork specifications were used to specify the induced draft fan in Section 5.2.1.4. Ductwork costs are given in Table 49.

5.2.1.6 Condensate Collection System. Criteria used for selection of the steam condensate collection system are as follows:

- For design purposes assume all steam that enters the building condenses
- Select a contaminated water storage tank sized to hold at least a 120 minute supply
- Select a potable water storage tank sized to hold at least a 60 minute supply
- A fabric filter bank and "Y" strainer are required to remove particulates
- Pump selection is based on the following
- a minimum inlet pressure into the fabric filter bank of 25 psig

TABLE 47. SUMMARY OF QUENCHER COST ESTIMATES

Steam Supply, lb/hr	Afterburner Exhaust, SCFM	Afterburner Flow,[a] ACFM	Quencher Cost[b] 1978$	Quencher Cost[c] 1984$	Estimated Column Height, ft	Estimated Refractory Height ft	Refractory Cost[d] 1984$	Pump Size,[e] gpm	Pump Cost,[f] 1984$	Water Supply Tank Cost,[g] 1984$	Quencher Total Cost, 1984$
15,000	9663	44,851	$19,000	$27,400	22	11	$1930	40	$2,260	$1,750	$33,340
10,000	6442	29,900	16,000	23,000	18	9	1260	25	2,200	1,750	28,210
5,000	3221	14,950	12,000	17,300	14	7	860	15	2,170	1,750	22,080

(a) At 2000 F.
(b) Journal Air Pollution Control Assoc. 28, No. 9, p. 965. Includes vessel, nozzle, and supports.
(c) 1984$ = 1978$ x (783.9/545.3).
(d) 90 percent alumina firebrick at $10.25/ft^2/inch x 1 inch x (πDL) x 1.09.
(e) Operates at 80 percent capacity, 100 psig supply pressure.
(f) Estimated by method described in Chemical Engineering, 2/22/81, pg. 115-8.
(g) 500 gallon molded polyethylene tank equipped with loose cover and stand. Cost from manufacturers brochure.

TABLE 48. ID FAN SPECIFICATION/COST

Flow SCFM	Fan Flow ACFM	ΔP Inches w.c.	Corrected[a] ΔP Inches w.c.	Fan Type	Class	Impeller Diam. In.	Fan[b] Cost 1980$	Fan[c] Dampers Cost 1980$	Required[d] hp	Selected Motor hp	Motor rpm	Motor[e] Cost 1980$	Starter[f] Cost 1980$	Fan System Cost 1980$	Fan[g] System Cost 1984$
15000	29,832	3.9	7.8	Backward Curved	II	40	$3600	$2400	37	50	1200	$ 1200	$ 500	$ 7700	$ 8390
10000	19,888	4.3	8.6	"	II	33	2800	1900	27	40	1800	600	400	5700	6210
5000	9,944	3.6	7.2	"	II	22	1500	1300	11	15	1800	300	250	3350	3650

(a) Corrected to operating temperature (see Chem. Eng., 5/18/81, pg. 171-7).
(b) CE 5/18/81. Includes 3 % for high temperature service (250-600 F).
(c) Outlet and inlet damper.
(d) hp = $v_{ACFM} \times \Delta P \times 3.152 \times 10^{-4}$.
(e) Drip-proof motor.
(f) Magnetic starter with circuit breaker.
(g) 1984$ = 1980$ x 1.09.

TABLE 49. DUCTWORK COSTS

Steam Flow, lb/hr	Item	Duct ID, Ft	Duct Length, Ft	Duct Cost(a) $/Ft	Duct Cost 1980$	Refrac Cost(b) 1980$	Elbow Cost(a) 1980$	Expan. Joint Cost(a) 1980$	Branch Cost(a) 1980$	Damper Cost 1980$	Total (c)Cost 1980$	Total Duct 1980$	Total Duct 1984$
15,000	Duct to AFB	2.0	10	$25	$250	--	$ 400	$2200	$700	--	$3550	$16,010	$17,450
	AFB to quencher	5.0	10	65	650	$1610	1400	3800	--	--	7460		
	Quencher to ID Fan	4.0	15	50	750	--	3000	--	--	--	3750		
	ID Fan to Stack	4.0	5	50	250	--	1000	--	--	--	1250		
19,000	Duct to AFB	1.5	10	20	200	--	300	1800	700	--	3000	12,990	14,160
	AFB to Quencher	4.0	10	50	500	1290	1000	3300	--	--	6090		
	Quencher to ID Fan	3.333	15	45	675	--	2250	--	--	--	2925		
	ID Fan to Stack	3.333	5	45	225	--	750	--	--	--	975		
5,000	Duct to AFB	1.25	10	20	200	--	300	1800	600	--	3000	10,470	11,410
	AFB to Quencher	3.0	10	40	400	970	600	2800	--	--	4770		
	Quencher to ID Fan	2.5	15	35	525	--	1500	--	--	--	2025		
	ID Fan to Stack	2.5	5	35	175	--	500	--	--	--	675		

(a) Chemical Engineering 12/29/80, pg. 71-3. 1/8" carbon steel plate, flanges every 40 ft.
(b) *One inch refractory (90 percent alumina)* @ $10.25/ft^2 inch x ($\pi$ x Duct ID x L).
(c) Automatic control.
(d) 1984$ = 1980$ x (784/721.3) = 1980$ x 1.09 (3rd Quarter 1984$).

- a pressure loss of 5 psig across the filter bank
- average vapor pressure of condensate over the decontamination treatment is 5 psia
- pressure is lost through five elbows (K_F = 0.9 each) and three half-open gate valves (K_F = 5.6 each)
- pipe length = 120 ft including an increase of 20 feet in elevation
- a 5 to 10 ft/sec flow velocity through the pipes.

The following equations were used to calculate the required pump pressure requirements:

$$h_F = (4FL/D + K_F)V^2/2g_c$$

$$\Delta P_{TOTAL} = \frac{60.1}{144}(g\Delta Z/g_c + h_F) + \Delta P_{FILTER}$$

The following are results of the calculations:

Water Flow, gpm	Pipe I.D., inches	Velocity, ft/sec	F	h_F, ftlbf/lbm	ΔP_{TOTAL}, psig
30	1.5	5.4	0.0045	17.5	41
20	1.0	8.2	0.0045	49.3	54
10	0.75	7.3	0.005	49.4	54

The pump pressure requirements were then used to cost the pump. The pump and tank costs are summarized in Table 50.

5.2.1.7 Steam Decontamination/Afterburner Cost Summary. A summary of the capital costs for the steam decontamination/afterburner thermal treatment system are given in Table 51.

5.2.2 Steam Decontamination/ Heat Exchanger System

The steam decontamination/heat exchanger system, illustrated in Figure 32b, consists of a packaged boiler, heat exchanger and a

TABLE 50. CONDENSATE COLLECTION SYSTEM COSTS

Steam Flow Rate, lb/hr	Condensate Flow Rate, gpm	Contaminated Water Tank Size, gal	Contaminated Water Tank Cost,[a] 1984$	Potable Water Tank Size, gal	Potable Water Tank Cost,[b] 1984$	Centrifugal Pump Cost,[c] 1984$	Filter Assembly Cost, 1984$	Valves, Strainer, Misc.[d] 1984$	Total Cost, 1984$
15,000	30	4000	$5,680	2,000	$2,520	$3,330	$1,500	$2,500	$15,530
10,000	20	2500	4,100	1,500	2,100	3,040	1,500	2,500	13,240
5,000	10	1500	3,150	750	1,790	2,770	1,500	2,500	11,710

(a) Flat top, cone bottomed, vertical, 304 stainless steel. 1984$ = 1982$ x 783.9/745.6 (see Chem. Eng. 4/5/82 p. 84).
(b) 304 stainless steel, vertical, flat-top and bottom (see Chem. Eng. 4/5/82, p. 85).
(c) 304 stainless steel centrifugal pump with motor (see Chem. Eng. 3/24/69, p. 126).
(d) Includes estimated cost of a carbon filter assembly for a vent on the contaminated water tank.

TABLE 51. STEAM DECONTAMINATION/AFTERBURNER EQUIPMENT COST SUMMARY

Item	Size	Steam Flow Rate, lb/hr 5,000	10,000	15,000
Boiler Package	26.5 MM Btu/hr/15,000 lb/hr	-	-	115,500*
Boiler Package	17.7 MM Btu/hr/10,000 lb/hr	-	92,400*	-
Boiler Package	8.8 MM Btu/hr/5,000 lb/hr	59,400*	-	-
Afterburner System	9,700 scfm/2,000 F/0.5 sec	-	-	42,400
Afterburner System	6,400 scfm/2,000 F/0.5 sec	-	34,700	-
Afterburner System	3,200 scfm/2,000 F/0.5 sec	29,100	-	-
ID Fan	30,000 acfm/3.9 inches water	-	-	8,400
ID Fan	20,000 acfm/4.3 inches water	-	6,200	
ID Fan	10,000 acfm/3.6 inches water	3,700	-	-
Ductwork	Carbon steel	-	-	17,500
Ductwork	Carbon steel	-	14,200	-
Ductwork	Carbon steel	11,400	-	-
Stack	36 inches ID/20 ft height	-	-	3,300
Stack	30 inches ID/20 ft height	-	3,100	-
Stack	20 inches ID/20 ft height	2,500	-	-
Quencher	45,000 acfm/22 ft height	-	-	33,300
Quencher	30,000 acfm/18 ft height	-	28,200	-
Quencher	15,000 acfm/14 ft height	22,100	-	-
Condensate Collection System	30 gpm/4,000 gal/2,000 gal	-	-	15,500
Condensate Collection System	20 gpm/2,500 gal/1,500 gal	-	13,200	-
Condensate Collection System	10 gpm/1,500 gal/750 gal	11,700	-	-
Sampling/Miscellaneous	--	15,000	15,000	15,000
	Total Purchased Equipment Cost (PEC)	$154,900	$207,000	$250,900
*Shop assembled	Installation, instrumentation, piping and electrical at 100% of PEC (less boiler cost)	95,500	114,600	135,400
	Total Capital Cost	$249,400	$321,600	$386,300

condensate collection system. The heat exchanger serves to condense the water vapor exhausted from the building such that the condensate can be recycled to the boiler. Because of potential restrictions on the use of large quantities of water, air cooled rather than water cooled heat exchangers were evaluated. A summary of the calculations given in Table 52 indicates that the heat exchanger required to condense the steam exhausted from the building at the worst conditions is cost prohibitively too large. Similar calculations using water rather than air as the coolant indicate that from 75 to 226 gpm of water are required for cooling.* These high water flow rates are not desirable. As such, the steam decontamination/heat exchanger concept is eliminated from further evaluation.

5.2.3 Steam Decontamination/Partial Recycle System

The steam decontamination/partial recycle system, illustrated in Figure 32c, consists of a packaged boiler, steam superheater, induced draft fan, air-cooled heat exchanger, and a condensate collection system. A mass balance on the system is shown in Figure 33. For the mass balances, it was assumed that one-half of the exhausted steam would be recycled to the building after superheating to 600 F. Less recycle would require the use of a larger and more costly heat exchanger. More recycle would result in either a more lengthy decontamination time because of reduction in the primary boiler size or a more costly boiler/heater combination.

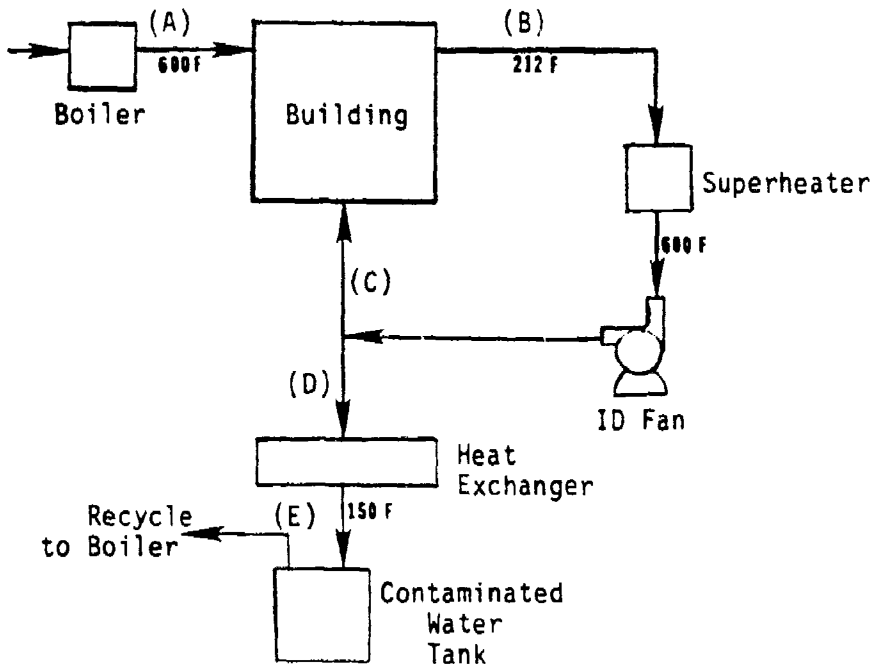
The specifications of components of the steam decontamination/ partial recycle system is as follows.

* For the worst case of steam exhausted from the building at a temperature of 212 F, the cooling water will not appreciably boil.

TABLE 52. SUMMARY OF CALCULATIONS FOR THE STEAM DECONTAMINATION/HEAT EXCHANGER SYSTEM

Building Exhaust Steam Flow Rate, lb/hr	Maximum Outlet Temperature[a], F	Steam Sensible Heat[b], Btu/lb	Heat Duty, MM Btu/hr	ΔT_{lm}	Heat Exchanger Area[e], ft^2	Required Cooling Air Flow Rate, scfm
15,000	516	1,127	16.9	169[c]	20,000	60,641
10,000	496	1,119	11.2	161[c]	13,913	40,188
5,000	405	1,072	5.4	142[d]	7,606	24,759

(a) From the building heat balances. Assumes a steam inlet temperature of 600 F.
(b) Amount of heat removal required to cool the steam at the maximum outlet temperature to liquid water at 200 F.
(c) Assumes inlet cooling air at 70 F, outlet air at 300 F.
(d) Assumes inlet cooling air at 70 F, outlet air at 250 F.
(e) For an overall heat transfer coefficient of 5 $Btu/ft^2/hr/F$ (condensing steam/air - see pp. 3-432 of Standard Handbook of Engineering Calculation, T. G. Hicks Editor, 1972).



Overall Steam Flow Rate, lb/hr	Flow at (A), lb/hr	Flow at (B), lb/hr	Flow at (C), lb/hr	Flow at (D), lb/hr	Flow at (E), gpm
15,000	7,500	15,000	7,500	7,500	15.6
10,000	5,000	10,000	5,000	5,000	10.4
5,000	2,500	5,000	2,500	2,500	5.2

Figure 33. Steam Mass Balances for the Steam Decontamination/Partial Recycle System

5.2.3.1 Boiler. The boiler was specified using the criteria given in Section 5.2.1.1. Costs for the 7,500 and 5,000 lb/hr units were estimated using the method given in Table 44. The boiler for the 2,500 lb/hr unit was estimated from data given in Means Construction Cost Data, 1984 edition. In all cases, the costs included materials and installation.

5.2.3.2 Superheater. The following criteria were used to specify the superheater:

- Normal operation at 75 percent capacity
- Gas/oil fired
- Stainless steel tubes

Specifications/costs for the superheaters are given in Table 53.

5.2.3.3 Heat Exchanger. The specification and costs for the heat exchanger are given in Table 54.

5.2.3.4 ID Fan/Ductwork. The ductwork and ID fan were specified and costed using the methods previously described in Section 4.2.4.1.

5.2.3.5 Condensate Collection System. The condensate collection system was specified using the method described in Section 5.2.1.6.

5.2.3.6 Steam Decontamination/PartialRecycle Cost Summary. A summary of the capital costs for the steam decontamination/ partial recycle system are given in Table 55.

5.2.4 Steam Decontamination/Packed Bed System

The steam decontamination/packed bed system, illustrated in Figure 32d, consists of a packaged boiler, packed bed, ID fan, stack, and condensate collection system. The boiler and condensate collection system are identical to the systems described in Sections 5.2.1.1 and

TABLE 53. SUPERHEATER SPECIFICATIONS/COSTS

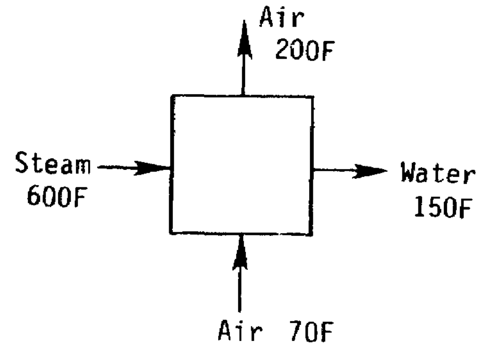
Steam Flow Rate, lb/hr	Required Heat Duty[a], MM Btu/hr	Selected Heat Duty[b], MM Btu/hr	Cost[c], 1968$	Cost[d], 1984$
15,000	2.8	3.7	$22,500	$64,580
10,000	1.9	2.5	16,500	47,360
5,000	0.9	1.2	8,250	23,680

(a) ΔH = Steam at 600 F - Steam at 212 F = 1335.2 - 1150.5 = 184.7 Btu/lb.
(b) Normal operation at 75 percent of capacity.
(c) Field erected, includes an additional 50 percent for stainless steel tubes (see Chem. Eng. 3/24/69, p. 121).
(d) 1984$ = 1968$ x 733.9/273.1.

TABLE 54. HEAT EXCHANGER SPECIFICATIONS/COSTS

Steam Flow Rate, lb/hr	Required Heat Removal[(a)], MM Btu/hr	Heat Exchanger Area[(b)], ft^2	Cooling Air Required, SCFM	Heat Exchanger Cost[(c)], 1984$	Heat Exchanger Fan Cost[(d)], 1984$	Total Heat Exchanger Cost, 1984$
7,500	9.13	4,588	57,960	$93,020	$20,820	$113,840
5,000	6.09	3,060	38,660	64,550	13,200	77,740
2,500	3.04	1,528	19,300	36,350	9,050	45,400

(a) ΔH = 1335.2-1150.5 + 970.3 + 62) = 1,217 Btu/lb.
(b) Assumes an overall U = 10 $Btu/ft^2/hr/F$ (see pp. 3-432 of Standard Handbook of Engineering Calculations, T. G. Hicks Editor) and the following stream temperatures:



$\Delta T_{lm} = 199$

(c) See Chemical Engineering 1/25/82, p. 104.
(d) For a 5-inch system pressure loss (see Chemical Engineering 5/18/81, p. 171-7).

TABLE 55. STEAM DECONTAMINATION/PARTIAL RECYCLE EQUIPMENT COST SUMMARY

Item	Size	Overall Steam Flow Rate, lb/hr 5,000	10,000	15,000
Boiler Package	13.4 MM Btu/hr/7,500 lb/hr	-	-	72,600*
Boiler Package	8.9 MM Btu/hr/5,000 lb/hr	-	59,400*	-
Boiler Package	4.5 MM Btu/hr/2,500 lb/hr	34,000*	-	-
Steam Superheater	3.7 MM Btu/hr/15,000 lb/hr	-	-	64,600
Steam Superheater	2.5 MM Btu/hr/10,000 lb/hr	-	47,400	-
Steam Superheater	1.2 MM Btu/hr/5,000 lb/hr	23,700	-	-
Heat Exchanger	4,590 ft^2/58,000 scfm	-	-	113,800
Heat Exchanger	3,060 ft^2/39,000 scfm	-	77,700	
Heat Exchanger	1,530 ft^2/19,000 scfm	45,400	-	-
ID Fan	10,000 scfm/11 inches water	-	-	24,900
ID Fan	6,700 scfm/11 inches water	-	19,300	-
ID Fan	3,300 scfm/11 inches water	13,700	-	-
Ductwork	Carbon steel	-	-	7,200
Ductwork	Carbon steel	-	6,200	-
Ductwork	Carbon steel	4,800	-	-
Condensate Collection System	15 gpm/2,000 gal/1,000 gal	-	-	10,900
Condensate Collection System	10 gpm/1,500 gal/750 gal	-	10,500	-
Condensate Collection System	5 gpm/750 gal/500 gal	9,400	-	-
Sampling/Miscellaneous	--	15,000	15,000	15,000
	Total Purchased Equipment Cost (PEC)	$146,000	$235,500	$309,000
*Shop assembled	Installation, instrumentation, piping and electrical at 100% of PEC (less boiler cost)	112,000	176,100	236,400
	Total Capital Cost	$258,000	$411,600	$545,400

5.2.1.6, respectively. The ID Fan, Ductwork, and Stack were specified in the method previously described in Section 4.2.4.1. The packed bed is described as follows.

5.2.4.1 Packed Bed. Results from a literature review indicate gamma alumina is a catalyst for GB agent decomposition through a hydrolytic mechanism[19,20] or by dealkylation.[21] The reaction rate is enhanced by the presence of water vapor and an increase in reaction temperature. The conditions of the building exhaust stream (i.e. water vapor at about 212 F) would be conducive for the catalytic decomposition of trace quantities of GB and probably VX and HD on gamma alumina.

The following served as the basis for specification of the packed column:

- One second residence time
- Because an induced draft fan was selected to maintain the building under a slight negative pressure, as small a pressure drop through the packed bed as possible is preferred. For design purposes, a pressure drop of about one inch water column per foot of column packing was selected
- For a worst case flow rate no condensation in the packed bed was assumed
- A damper/duct is used to supply air downstream of the packed bed in order to maintain a constant volumetric flow rate and constant pressure drop through the system
- The pressure drop through the distributor plate is one-third the pressure drop of the entire column
- One standby unit is required
- Column height is 10 feet
- The density of the alumina packing is equivalent to one inch ceramic Raschig rings

The pressure drop through a counter-current liquid (i.e., condensate) and gas (i.e., steam) packed bed can be estimated by the following equation*:

---

* See Chemical Engineers Handbook, 5th Ed. Edited by Perry and Chilton, pg. 18-22.

$$\Delta P = C_2 10^{(C_3 U_L)} \rho_g U_g^2$$

where $-C_2 = 0.80$, $C_3 = 0.0348$ for 1 inch Raschig rings

$-U_1$ is much less than one, therefore $10^{(C_3 U_1)} \approx 1$

$- \rho_g = 0.0373$ lb/ft^3 (steam at 212 F)

$- \Delta P$ = pressure drop per foot of packing, inches of water

$-U_g$ = superficial gas velocity = $v/(\pi D^2/4)$, ft/sec

Results of the calculations are given in Table 56a. Estimated costs for the packed columns are given in Table 56b.

5.2.4.2 Steam Decontamination/Packed Bed Cost Summary. A summary of the estimated capital costs for the steam decontamination/packed bed system are given in Table 57.

5.3 Steam Decontamination Cost Summary

A summary of the operating costs for the steam decontamination concept as applied to Buildings 1, 2 and 3 are given in Table 58 through 60, respectively. The basis for estimation of the operating costs is given in Section 4.3.2.

A summary of the total cost (i.e., operating and capital) for the three evaluated steam decontamination methods is given in Table 61 and illustrated on Figure 34.

5.4 Steam Decontamination Recommendations/Conclusions

Results of the engineering analysis indicates that the use of the steam decontamination concept for decontaminating field structures is feasible. Based on the economic analysis the recommended features of the steam decontamination concept are:

- Boiler sized at about 5,000 lb/hr of 250 psig steam superheated to 632 F

TABLE 56. PACKED COLUMN SPECIFICATIONS/COSTS

Table 56a. Pressure Drop in the Packed Column

Steam Flow Rate, lb/hr	Steam Flow Rate, acfm	Cross-Sect. Area Required for ΔP =1 in./ft, ft^2	Number of 3 ft Diam. Columns Required(a)	Actual ΔP, in./ft of Column Ht	ΔP Across Distributer Plate, in. of water	Total ΔP of column,(b) in. of water
15,000	6,702	19.3	4	0.83	4.1	12.4
10,000	4,468	12.8	3	0.83	4.1	12.4
5,000	2,234	6.4	2	0.83	4.1	12.4

(a) Includes one standby column
(b) For a 10 ft column

Table 56b. Cost of the Packed Column

Steam Flow Rate, lb/hr	Number of Beds Required	Inside Diam., ft	Packed Column Cost(a), 1984$	Pump Size(b), gpm	Pump Cost(c) 1984$	Total Packed Column Cost, 1984$
15,000	4	3	$133,880	30	$3,330	$137,160
10,000	3	3	100,410	20	3,040	103,450
5,000	2	3	66,940	10	2,770	69,710

(a) Cost for 2-5 ft sections of a double bed 304 stainless steel column rated at +25 psig to full vacuum and a 350 F operating temperature is $29,000 (1982$). Packing is estimated as $30/ft^3$(1982$) so the total cost of one packed bed is $31,830 (1982$) = $33,470 (1984$) (see Chem. Eng., 4/5/82, p 103).
(b) A pump is used to transfer condensate from the column to the contaminated water storage tank. The pump was sized based on the worst case flow rate (i.e., all steam condenses).
(c) See Table 50.

TABLE 57. STEAM DECONTAMINATION/PACKED BED TREATMENT COST SUMMARY

Item	Size	Steam Flow Rate, lb/hr 5,000	10,000	15,000
Boiler Package	26.5 MM Btu/hr/15,000 lb/hr	-	-	115,500*
Boiler Package	17.7 MM Btu/hr/10,000 lb/hr	-	92,400*	-
Boiler Package	8.8 MM Btu/hr/5,000 lb/hr	59,400*	-	-
Packed Bed	4-3 ft x 10 ft beds, 304 S.S.	-	-	137,200
Packed Bed	3-3 ft x 10 ft beds, 304 S.S.	-	103,500	-
Packed Bed	2-3 ft x 10 ft beds, 304 S.S.	69,700	-	-
ID Fan	6,700 acfm/30 inches water	-	-	23,400
ID Fan	4,468 acfm/30 inches water	-	18,600	
ID Fan	2,234 acfm/30 inches water	12,700	-	-
Ductwork	Carbon steel	-	-	8,100
Ductwork	Carbon steel	-	6,400	-
Ductwork	Carbon steel	5,000	-	-
Stack	18 inches ID/20 ft height	-	-	2,300
Stack	15 inches ID/20 ft height	-	2,000	-
Stack	10 inches ID/20 ft height	1,500	-	-
Condensate Collection System	30 gpm/4,000 gal/2,000 gal	-	-	15,500
Condensate Collection System	20 gpm/2,500 gal/1,500 gal	-	13,200	-
Condensate Collection System	10 gpm/1,500 gal/750 gal	11,700	-	-
Sampling/Miscellaneous	--	15,000	15,000	15,000
	Total Purchased Equipment Cost (PEC)	$175,000	$251,100	$317,000
*Shop assembled	Installation, instrumentation, piping and electrical at 100% of PEC (less boiler cost)	115,600	158,700	201,500
	Total Capital Cost	$290,600	$409,800	$518,500

TABLE 58. OPERATING COSTS FOR BUILDING 1

Steam Flow Rate, lb/hr	T_{IN}, F	Insulation, inches	Decon Time, hrs	Boiler CH_4, 1000 scf	CH_4 Cost(b)(c), 1984$	Electrical Cost(d), 1984$	Operators(e), 1984$	Building Preparation, 1984$	Cleanup(e), 1984$	Total, 1984$
5,000	600	2	(a)	-	-	-	-	-	-	-
5,000	600	4	183	1,214	$4,910	$300	$22,020	$ 59,280	$21,690	$108,200
5,000	600	12	140	929	3,760	300	16,850	161,800	31,790	214,500
10,000	600	2	99	1,314	5,310	650	11,920	45,900	16,290	80,070
10,000	600	4	82	1,089	4,400	650	9,870	59,280	21,690	95,890
10,000	600	12	74	982	3,970	650	8,910	161,800	31,790	207,120
15,000	600	2	66	1,314	5,310	1000	7,950	45,900	16,290	76,450
15,000	600	4	59	1,115	4,510	1000	7,100	59,280	21,690	93,580
15,000	600	12	55	1,095	4,430	1000	6,620	161,800	31,790	205,640

(a) Building is not decontaminated after 300 hours of operation.
(b) $4.04/1000 scf (Energy User News, 11/19/84).
(c) Additional CH_4 cost of 68 percent required for the Steam Decontamination/Afterburner System while a CH_4 credit of 35 percent is allowed for the Steam Decontamination/Partial Recycle System.
(d) Estimated
(e) See Section 4.3.2.

TABLE 59. OPERATING COSTS FOR BUILDING 2

Steam Flow Rate, lb/hr	T_{IN}, F	Insul., inches	Decon Time[a], hrs	Boiler[a] CH_4, 1000 scf	CH_4 Cost[c][d], 1984$	Electrical Cost[e], 1984$	Operators[f], 1984$	Building[f] Preparation, 1984$	Cleanup[f], 1984$	Total, 1984$
5,000	600	2	(b)	-	-	-	-	-	-	-
5,000	600	4	636	4,218	$17,040	$1,000	$76,540	$22,580	$11,590	$128,750
5,000	600	12	435	2,886	11,660	1,000	52,350	52,570	25,670	143,250
10,000	600	2	729	9,678	39,100	2,000	87,740	15,090	8,070	152,000
10,000	600	4	423	5,616	22,690	2,000	50,910	22,580	11,590	109,770
10,000	600	12	324	4,302	17,380	2,000	38,990	52,570	25,670	136,610
15,000	600	2	555	11,049	44,640	3,000	66,790	15,090	8,070	137,590
15,000	600	4	354	7,047	28,470	3,000	42,600	22,580	11,590	108,240
15,000	600	12	282	5,616	22,690	3,000	33,940	52,570	25,670	137,870

(a) For 3 floors.
(b) Each floor of the building requires more than 300 hours of decontamination time.
(c) $4.04/1000 scf (Energy User News, 11/19/84).
(d) Additional CH_4 cost of 68 percent required for the Steam Decontamination/Afterburner System With a CH_4 credit of 35 percent allowed for the Steam Decontamination/Partial Recycle System.
(e) Estimated
(f) See Section 4.3.2.

TABLE 60. OPERATING COSTS FOR BUILDING 3

Steam Flow Rate, lb/hr	T_{IN}, F	Insul., inches	DECON Time, hrs	Boiler CH_4, 1000 scf	CH_4 Cost[a][b], 1984$	Electrical Cost[c], 1984$	Operators[d], 1984$	Building[a] Preparation, 1984$	Cleanup[d], 1984$	Total, 1984$
5,000	600	2	126	836	$3,380	$250	$15,160	$ 8,500	$ 6,750	$34,040
5,000	600	4	69	458	1,850	250	8,300	10,700	8,950	30,050
5,000	600	12	55	365	1,470	250	6,620	19,500	17,750	45,590
10,000	600	2	49	621	2,510	500	5,900	8,500	6,750	24,160
10,000	600	4	39	494	2,000	500	4,690	10,700	8,950	26,840
10,000	600	12	35	444	1,790	500	4,210	19,500	17,750	43,750
15,000	600	2	36	717	2,900	750	4,330	8,500	6,750	23,230
15,000	600	4	31	617	2,490	750	3,730	10,700	8,950	26,620
15,000	600	12	29	577	2,330	750	3,490	19,500	17,750	43,820

(a) $4.04/1000 scf (Energy User News, 11/19/84).
(b) Additional CH_4 cost of 68 percent required for the Steam Decontamination/Afterburner System With a CH_4 credit of 35 percent allowed for the Steam Decontamination/Partial Recycle System.
(c) Estimated
(d) See Section 4.3.2.

TABLE 61. STEAM DECONTAMINATION CONCEPT COST SUMMARY

Steam Flow Rate, lb/hr	Insul. Inches	Operating Cost ($1000)[b]				Total Cost ($1000)[b]		
		Building 1	Building 2	Building 3	Total Operating Cost	Afterburner	Partial Recycle	Packed Bed
5,000	2	(a)	-	-	-	-	-	-
5,000	4	$108.2	$128.8	$30.1	$267.1	$516.5	$525.1	$557.7
5,000	12	214.5	143.3	45.6	403.4	652.8	661.4	694.0
10,000	2	80.1	152.0	24.2	256.3	577.9	667.9	666.1
10,000	4	95.9	109.8	26.8	232.5	554.1	644.1	642.3
10,000	12	207.1	136.6	43.8	387.5	709.1	799.1	797.3
15,000	2	76.5	137.6	23.2	237.3	623.6	782.7	755.8
15,000	4	93.6	108.2	26.6	228.4	614.7	773.8	746.9
15,000	12	205.6	137.9	43.8	387.3	773.6	932.7	905.8

(a) Building is not decontaminated after 300 hours of operations.
(b) 1984$.

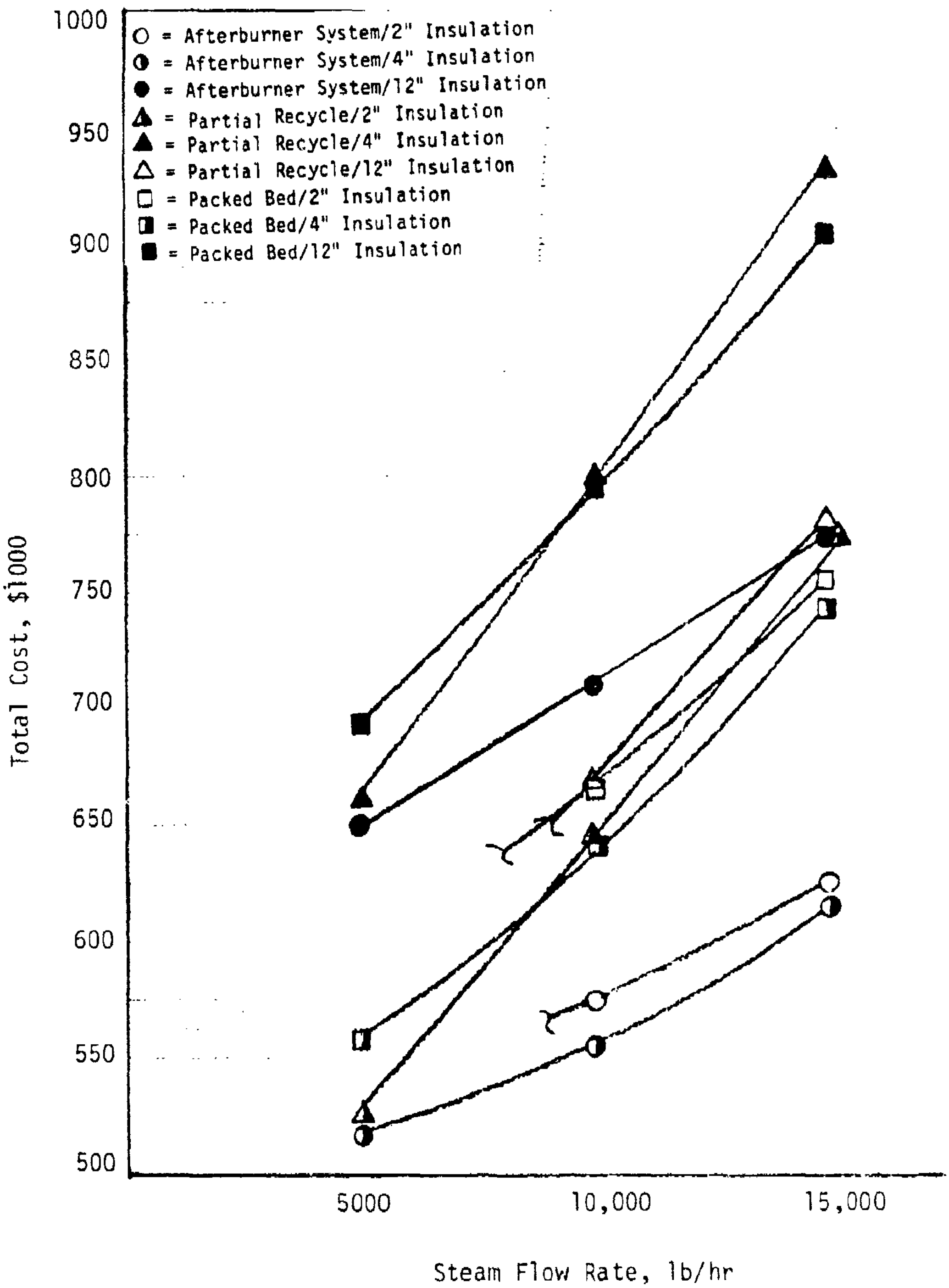


FIGURE 34. STEAM DECONTAMINATION COST SUMMARY

- An afterburner/quencher system to decontaminate uncondensed steam exhausted from the building
- Induced draft fan to maintain the building under a negative pressure during operations
- Insulation on the exposed building surfaces equivalent to R = 80

It is important to note that the afterburner system is preferred over the partial recycle system because a negative pressure can be maintained inside the building with the afterburner system while not with the partial recycle system. A negative building pressure is desirable to minimize the potential for agent leakage.

A preliminary piping and instrumentation diagram is given in Figure 35 while a conceptualization is shown in Figure 36.

6.0 CONCLUSIONS/RECOMMENDATIONS

Results of the engineering analyses demonstrate the feasibility of application of the hot gas and steam concepts to decontaminate field structures contaminated with GB, VX, or HD. Equipment for field application of either concept is commercially available on an off-the-shelf basis (i.e., no special equipment designs are anticipated).

Features of the preferred hot gas decontamination system include the following:

- 7 million Btu/hr burner hot gas supply
- After burner for treatment of the building exhaust stream
- Quencher to cool the afterburner exhaust gas
- Induced draft fan to maintain the building under a negative pressure during operaitons
- OPAB or other decontaminant as a protective coating on the external building surfaces
- Insulation on the exposed building surfaces equivalent to R=40.

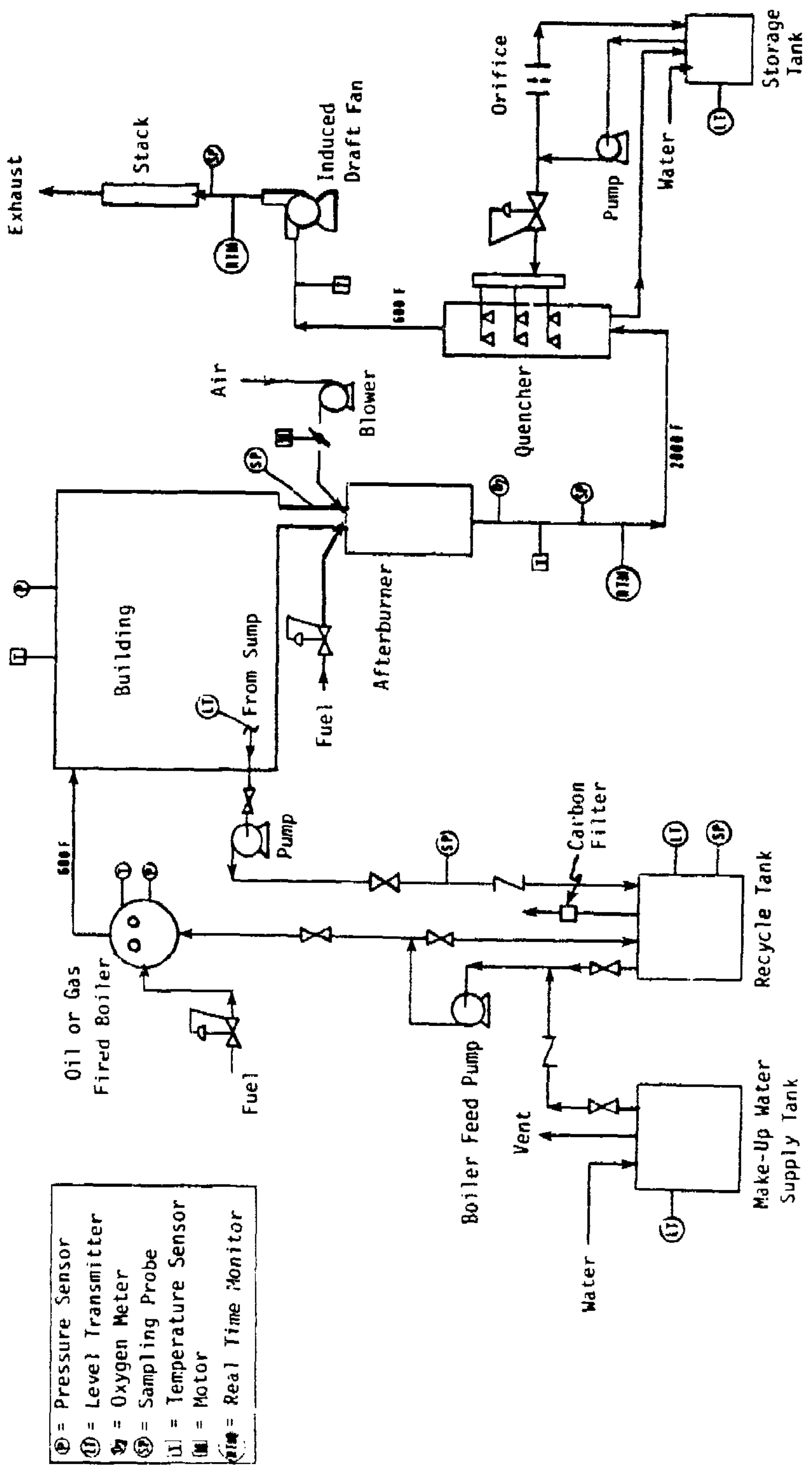


FIGURE 35. PRELIMINARY P&I DIAGRAM OF THE STEAM DECONTAMINATION CONCEPT

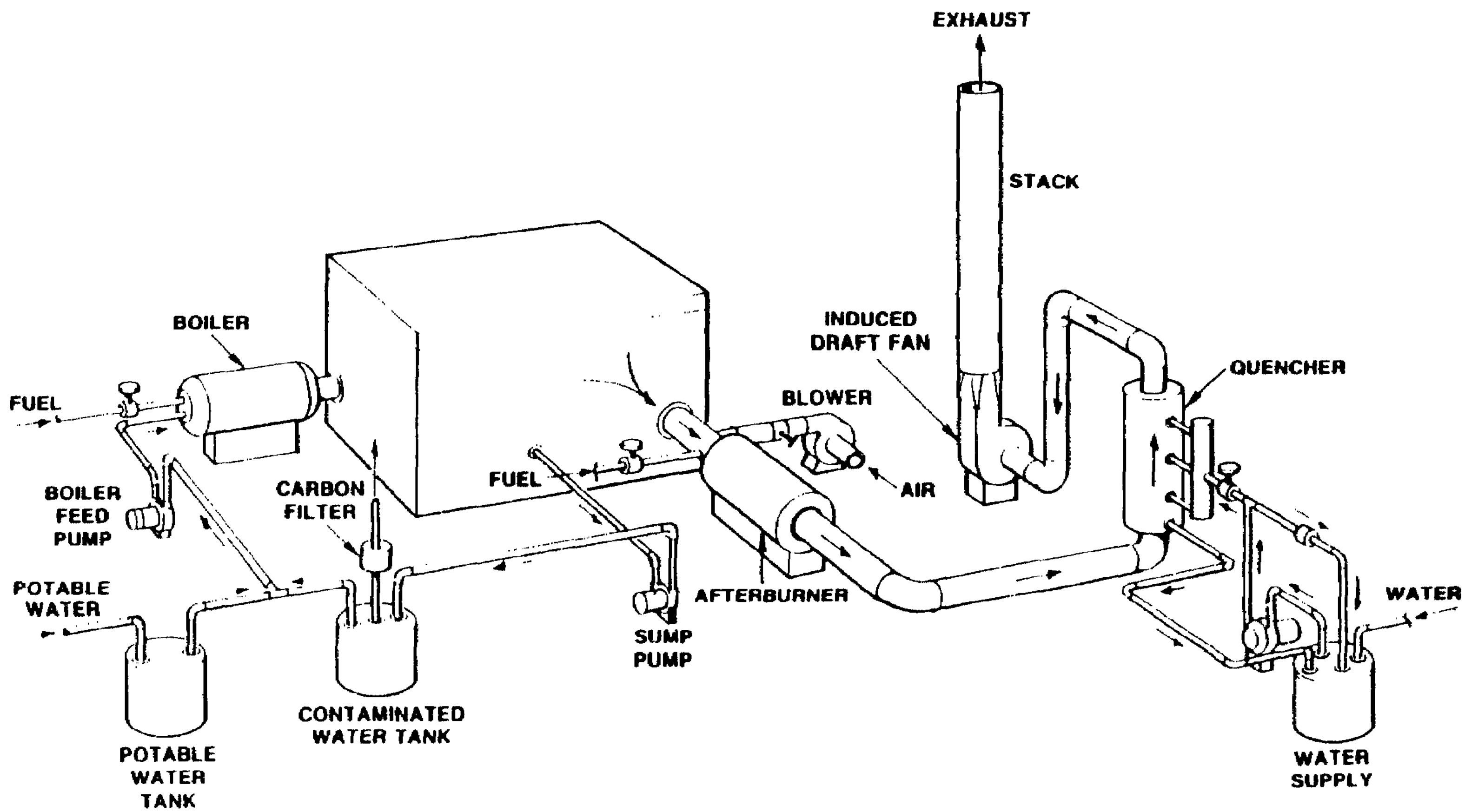


FIGURE 36. CONCEPTUALIZATION OF THE STEAM DECONTAMINATION CONCEPT

A literature analysis of the thermal effects on concrete indicated that during the hot gas treatment, the concrete should not be heated to a temperature greater than about 400 C (752 F). Also, following cool-down, the concrete should be wetted with water to regain most of the strength lost during the heat treatment.

Features of the preferred steam decontamination system include the following:

- Boiler sized at 5000 lb/hr of 250 psig steam superheated to 632 F
- Afterburner/quencher to treat uncondensed steam exhausted from the building
- OPAB or other decontaminant as a protective coating on the external building surfaces
- Insulation on the exposed building surfaces equivalent to R = 30
- Recycle of condensate through the boiler.

Results of the cost analyses on the preferred decontamination systems are as applied to the model facility are given below:

Decontamination System	Capital Cost,* $1000	Operating Cost,* $1000	Total Cost,* $1000
Hot Gas	$180	$167	$347
Steam	$249	$267	$516

The costs indicate that the hot gas decontamination concept is economically preferred over the steam decontamination concept.

*1984

7.0 REFERENCES

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APPENDIX VII

SUBTASK 9. FATE OF AGENT ON CONCRETE

SUMMARY REPORT

on

TASK 3 SUBTASK 9
FATE OF AGENT IN CONCRETE

by

B. C. Garrett and T. L. Hayes

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TEST REPORT

FOR

TASK 3 SUBTASK 9

TEST PLAN FOR FATE OF AGENT
ON CONCRETE

Contact No. DAAK11-81-C-0101

for

UNITED STATES ARMY

TOXIC AND HAZARDOUS MATERIALS AGENCY

1.0 INTRODUCTION

The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) has responsibility for decontamination of facilities contaminated with chemical agents. Battelle's Columbus Laboratories has been assisting USATHAMA in identifying, developing, and evaluating novel decontamination techniques for agent contaminated facilities. The current decontamination standard (the 5X condition) is not defined precisely in analytical terms. This deficiency can lead to ambiguity in assessing the effectiveness of decontamination procedures. A standard based on an analytical determination of residual agents on building surfaces and subsurfaces before and after decontamination is desirable to ensure compatibility with unrestricted use requirements.

1.1 Novel Processing Technology Program

Suitable analytical methods for use in the agent decontamination studies on this USATHAMA Contract (the "Novel Processing Technology Program") were unavailable when laboratory experiments were being initiated. Consequently, analytical method development, in accordance with USATHAMA Quality Assurance Program Plan guidance (1), was undertaken for the agents GB, HD, and VX on selected building materials.

Building materials examined included unpainted mild steel, unpainted stainless steel, and unpainted concrete. These same materials were also examined following painting with selected paints believed to be representative of those used in agent facilities. These paints included a typical alkyd paint and more specialized plasticized paints.

Attempts to recover agents by solvent extraction from the painted and unpainted materials were successful and produced no unanticipated results. The typical analytical method used for this solvent extraction and subsequent analysis is depicted in the flow diagram shown in Figure 1. Specific procedures that were investigated and experimental results that were obtained have been documented and reported to USATHAMA (2).

Use of the solvent extraction method depicted in Figure 1 proved significantly less successful for extraction of agents from concrete than for extractions of agents from metal. Assorted modifications to the basic method were tried, such as use of various solvents and crushing the concrete specimen to facilitate contact between agent and solvent. Results were disappointing, in that GB could not be extracted by any technique attempted at levels dosed significantly above the method detection limit. Agents HD and VX could be partially recovered (between 33 and 67 percent recovery) from unpainted concrete using acetonitrile as the extraction solvent and a 20-minute extraction cycle. However, the precision (repeatability) observed for this technique was extremely poor, and efforts to improve this repeatability were unsuccessful. These results for all three agents suggested that all or part of the agent applied to the concrete specimen was not available to be extracted due to interaction with the concrete. Several factors suggest that this interaction is the chemical reaction of hydrolysis occurring between the agent and concrete. These factors are:

- Agent recovery experiments were successful for metals but failed for concrete. This result implies that lack of recovery from concrete cannot be attributed to selection of extraction solvents having little or no attraction for agents.

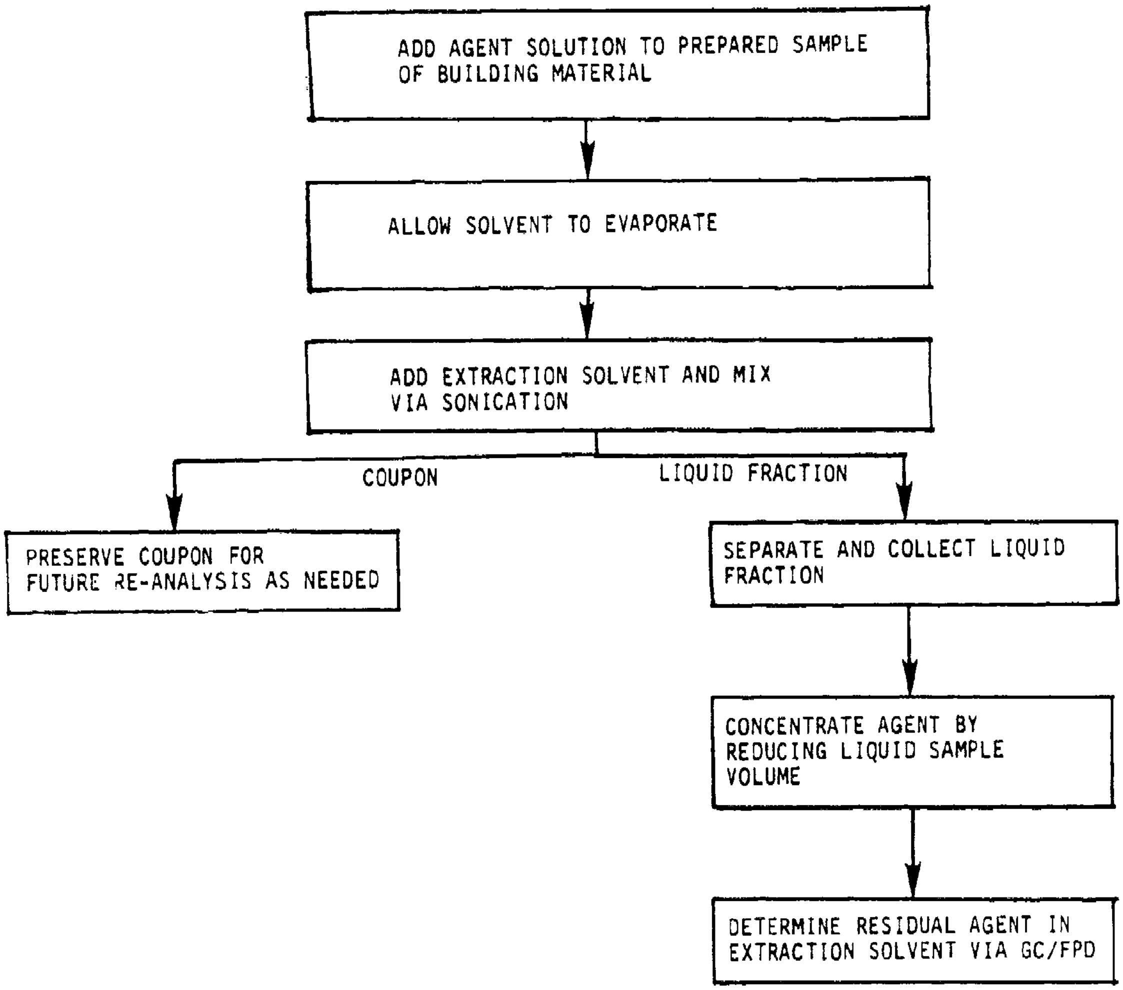


FIGURE 1. FLOW CHART FOR SOLVENT EXTRACTION OF AGENT FROM BUILDING MATERIAL

- Concrete provides a porous, reactive matrix; contains significant occluded water and waters of hydration; and is alkaline (with pH ranging typically from 12 to 13). These characteristics would favor hydrolysis.

- The agents GB, HD, and VX are very susceptible to chemical reaction under alkaline conditions (3).

On the basis of these factors, the literature pertaining to similar studies of agent interactions with concrete was surveyed for additional evidence as to the fate of agent on concrete.

1.2 Literature Survey Results

A survey of the technical literature was conducted to uncover experimental data regarding the fate of the agents GB, HD, and VX on concrete. This survey failed to uncover any evidence that the fate of these agents on concrete had previously been characterized such that the nature of any interaction between agent and concrete was precisely identified. Although no directly comparable experimental results were located, considerable data were found to support both the hypothesis that agent does interact with concrete and the contention that this interaction is a chemical reaction resulting in hydrolytic decomposition of the agent. The results of the technical literature survey are summarized in the following sections on each chemical agent.

1.2.1 Agent GB.

The persistence of GB (isopropyl methyl phosphonofluoridate) on various materials, including concrete, was investigated by Jackson in an effort to determine residual contact hazard resulting from agent contamination of surfaces (4). The experimental design specified use of five materials: sand, sandy loam, high humus loam, asphalt, and concrete. A chemical agent (GA or GB) was applied to the surface by an unspecified technique to give a contamination density 83 or 330 g/m^2.

The atmosphere above the surface was then sampled using impingers containing diethylphthalate, and the contents of the impingers were analyzed colorimetrically. Results are summarized in Figure 2. Jackson concluded that decontamination of the five materials evaluated would be unnecessary if more than 6 hours had elapsed since contamination had occurred. Because of the limited analytical resources available when Jackson carried out this study in the early 1950's and, the lack of precise agent separation and identification capabilities inherent in the colorimetric assay method used, the conclusions may be flawed. The results do demonstrate, however, the limited extent to which GB is released from concrete as well as from the other materials. The maximum recoverable GB from concrete was found by Jackson to be 30 percent (see Figure 2). Jackson did not provide any guidance as to the fate of the GB that remained on the concrete.

Two principal investigations do provide some guidance, however, and support the contention that hydrolysis accounts for this lack of GB recovery. These investigations are the work of Epstein and others on the fate of GB in seawater and similar ionic solutions (5,6) and the environmental fate studies conducted at U.S. Army Dugway Proving Ground (7,8).

Destruction of GB in seawater is pertinent to the prospect of GB hydrolysis on concrete surfaces due to similarities in chemical environment. For example, both seawater and concrete contain relatively high concentrations of hydroxy-metal complexes of Mg^{2+} and Ca^{2+}, and both seawater and concrete are in the alkaline pH range. Epstein has characterized the fate of GB in seawater and has determined this fate to be hydrolysis, with substantial participation by magnesium and calcium hydroxy complexes (5).

The dramatic effect on the hydrolysis rate of GB due to the participation of these alkali metals was further characterized by Epstein (6). Results indicated that the time for GB hydrolysis reaction half-life was reduced ten-fold for solutions containing Mg^{2+} and Ca^{2+} ions versus solutions of the same pH but without these alkali metal cations. The accelerative effect of alkali metals on GB hydrolysis has

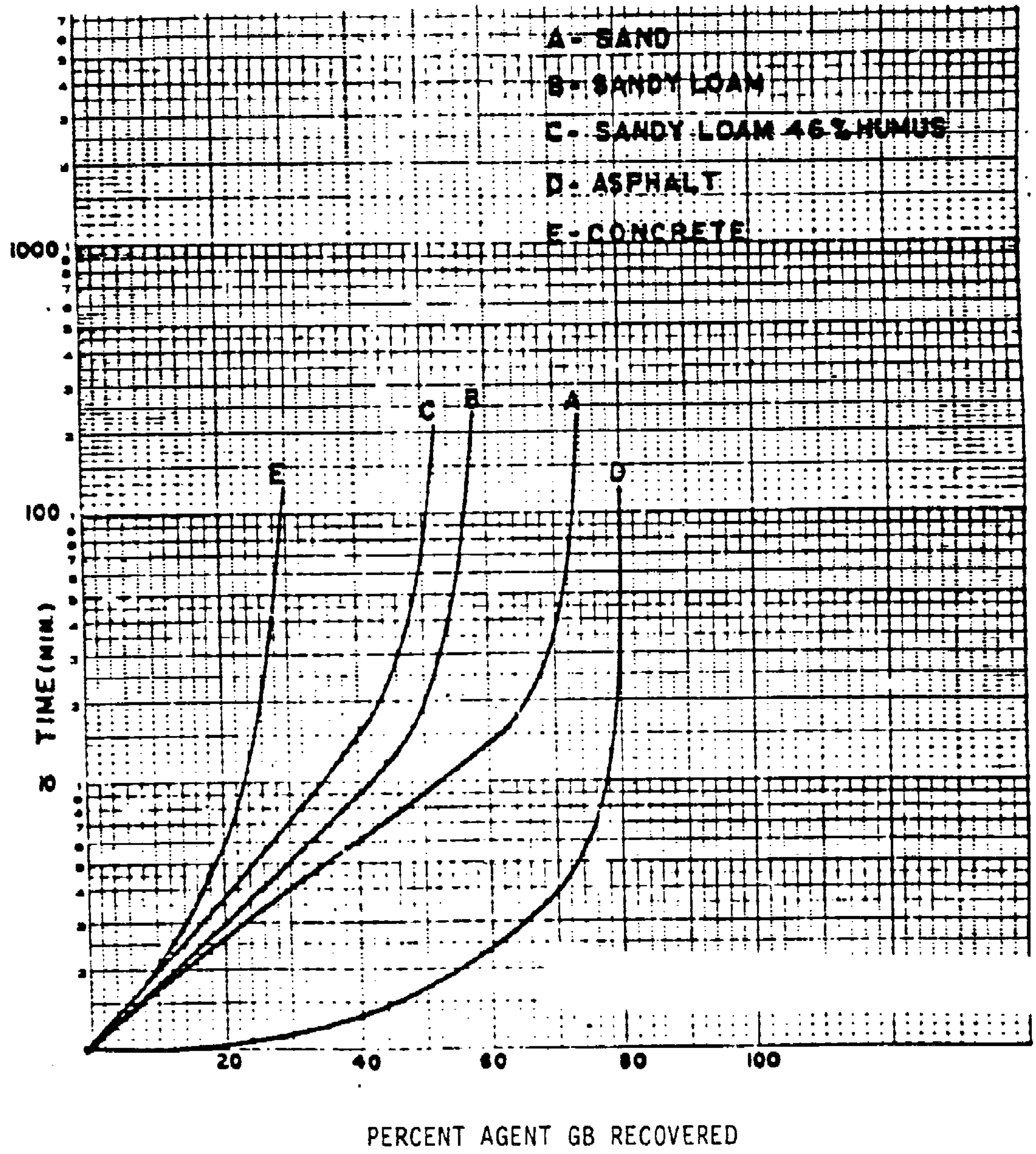


FIGURE 2. AGENT GB RECOVERY FROM VARIOUS MATERIALS(4)

an important inference for the fate of GB on concrete. Epstein's results have shown that the hydrolysis half-life for GB in brackish seawater at pH 13, a typical pH for concrete, is less than two seconds (< 0.03 minutes). Therefore, if GB hydrolysis does occur on concrete, the rate will be rapid.

The environmental fate of GB was studied at Dugway Proving Ground for conditions that offer parallels to conditions present in concrete. The investigations by Houle and his associates (7) focused on soil types and moisture contents in soil that resemble concrete. The soil types selected were representative of the dry lake bed and arid desert conditions characteristic of the Granite Peak area at Dugway. Consequently, the soils were mineral soils with insignificant humic content. Of the three soils used in this study, the Pickleweed soil would be most similar in physical and chemical characteristics to those of concrete, in that both have significant soluble salt content and are high in sand. Results showed the Pickleweed soil rapidly destroyed GB through alkaline hydrolysis. This same alkaline hydrolysis was observed for the two other soil types. The lifetime of GB in all three soils was determined to be brief such that little possibility existed for GB to persist in these soils. Subsequent soil sampling, extraction, and analysis from Granite Peak sites where substantial drainage of GB onto the ground had occurred confirmed both the absence of GB and the presence of known hydrolysis products in these soils (8).

1.2.2 Agent HD.

Persistence of HD (bis (2-chloroethyl) sulfide) on concrete and two other surface materials was investigated by Brady et al. in conjunction with studies of the all-purpose decontaminant (APD) (9). In this study, HD was deposited on concrete surfaces in drops approximately 500 microns in diameter. The concentration applied to the surface was approximately 10 g/m^2 of surface area. Decontamination treatment of the contaminated specimen consisted of a control (i.e., no added APD) plus three increasing application rates of APD. Results in terms of the percent agent that disappeared in various time intervals are summarized in

Table 1. As these data in Table 1 show, disappearance of HD in the absence of the decontaminant was 99 percent complete within 4 hours. The initial disappearance from the two porous surface materials, concrete and sand, was tenfold greater than that observed for the relatively nonporous aluminum, as seen by the results for percent HD lost within 0.25 hours.

In the presence of decontaminant, HD disappearance was slowed substantially for concrete. This decrease was insignificant for soil and was not observed for aluminum. Brady et al. attributed these results to inhibition of evaporation of HD from concrete following application of APD.[9] Unfortunately, this conclusion seems to

TABLE 1. DISAPPEARANCE WITH TIME OF HD ON VARIOUS SURFACES WITH AND WITHOUT APPLICATION OF APD (9)

Type of Surface	Contamination Level, g/m^2	Volume Ratio APD:HD	Percent Agent Lost in[a] 0.25 hr	1 hr	4 hr
Aluminum	5.0	No APD	5	34	>99
	4.8[b]	20:1	-	76	-
		25:1	90	95	99
		45:1	95	97	>99
Concrete	10.0	No APD	62	83	99
	3.8[b]	25:1	16	29	-
		45:1	34	34	63
		100:1	-	37	58
Soil	10.0	No APD	50	83	95
	5.0[b]	45:1	-	74	>99

a. Some of the data are the results of single determinations, and other are averages of duplicate determinations. In the experiments in which APD was added, the additions were made when the HD had been on the surface for 0.25 hr. For these experiments, the times listed are those subsequent to the additions of APD, and the percentages are based on the contamination levels given in the second column.

b. Calculated for the time of APD addition on the basis of the amount of HD found at this time in the absence of APD.

contradict the observation that disappearance of HD was faster from the porous materials, which should retard evaporation due to wicking or permeation of HD within the surface material, than from aluminum, where evaporation should be greater due to the enhanced exposure of HD to the atmosphere. Another explanation for this observed decrease in HD disappearance from concrete following application of APD might be that APD competed effectively with concrete for HD; that is, HD preferentially dissolved into the APD rather than permeating into the concrete. This explanation seems weak in view of the rapid HD disappearance observed for APD on aluminum. If HD were preferentially dissolved into APD, then the disappearance from concrete should be no less than that observed for either no APD or APD on aluminum.

A more plausible explanation for these results is that APD reacts with concrete and, thereby, neutralizes some of the alkaline hydrolysis ability of concrete with a corresponding loss in APD decontaminating ability. This explanation would also account for the corresponding decrease in the rate of reaction between APD and HD. APD (now known as CD-1) is composed of a mixture of lithium hydroxide, monoethanolamine, and propylene glycol. There is no apparent connection between this composition for APD and any corresponding reaction with concrete, and Brady et al. failed to examine the prospect that HD reacts with concrete. Consequently, the ultimate explanation for the results reported in Table 1 cannot be reached with the data provided. However, these results do support the likelihood that a reaction between HD and concrete does occur.

1.2.3 Agent VX.

Persistence of VX {O-ethyl S-[2-(diisopropylamino)ethyl methylphosphonothioate]} on concrete was studied by Brady et al. during the all-purpose decontaminant (APD) effort using the same experimental methods discussed previously for agent HD (9). Results obtained for VX on concrete were similar to those obtained for HD; that is, substantial loss of VX from concrete occurred in the absence of APD. These results are summarized in Table 2.

TABLE 2. DISAPPEARANCE OF VX FROM CONCRETE WITH AND WITHOUT APD (9)

Volume Ratio APD:VX	Exposure Time (hr)		Average Percent Agent Lost[a]
	Before APD	After APD	
No APD	0.2	N/A[b]	51
50:1	0.2	0.5	81
50:1	0.2	1.0	76
90:1	0.2	1.0	72

(a) Percentage based on initial contamination level of 10 g/m^2.
(b) N/A = not applicable.

Brady et al. offered two possible explanations for the recovery of 49 percent of the VX (that is, 51 percent lost) in the case of no APD being applied. These explanations are:

- Reaction between the agent and alkaline components of the concrete
- Inaccessibility of agent due to its sequestering in small pores of the concrete.

The post-contamination sample work-up procedure reported by Brady et al. required pulverizing the concrete and stirring the resultant mixture of pulverized concrete and the extraction solvent, a tris(hydroxymethyl) methylamine buffer solution. This process should have ensured good contact between agent and solvent. Unfortunately, Brady et al. failed to pursue this issue of the fate of VX on concrete; and the analytical procedure used (enzymatic assay) to quantify residual agent was incapable of resolving, identifying, and quantifying potential hydrolysis products.

The kinetics and mechanisms of VX hydrolysis have been examined extensively; findings have been summarized by Epstein et

al. (10), who have derived a rate equation to account for VX hydrolysis in the pH range of 1.0 to 13.5. This equation is:

$$k_{obs} = k_{H_2O}\frac{[H^+]}{Ka+[H^+]} + k\,\frac{Ka}{Ka+[H^+]} + k_{OH}[OH^-]\frac{Ka}{Ka+[H^+]}$$

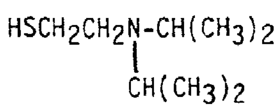
where:

k_{H_2O} = $2.9 \times 10^{-4} hr^{-1}$ (first-order rate constant)
k = $1.5 \times 10^{-2} hr^{-1}$ (first-order rate constant)
k_{OH} = $30\ M^{-1}hr^{-1}$ (second-order rate constant)
K_a = 2.5×10^{-9} (acid dissociation constant)

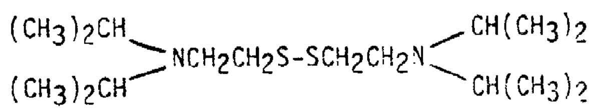
The first term in this equation ($k_{H_2O}[H^+]/(Ka + [H^+])$) is the major contributor to the overall reaction rate up to pH 6.5. The second term in this equation ($k\ Ka/(Ka + [H^+])$) is the dominant term in the pH range 6.5 to 10. This term represents the kinetics of the simultaneous cleavage of the P-S, O-C and S-C bonds. The final term in this equation is the controlling factor in the kinetics of hydrolysis above pH 10.0. In this range, cleavage of P-S bond accounts for the complete hydrolysis reaction.

The conclusion to be drawn from this equation is that cleavage of the P-S bond predominates for VX hydrolysis within the pH range expected for concrete (pH 12-13). The observed rate constant, for this pH range is 0.3 to 2.5 $hours^{-1}$.

Evidence that VX undergoes hydrolysis when applied to concrete-like materials can be found in the assorted investigations of the fate of VX on soils. Both Kraaijk et al. (11,12) and Verweij (13) have studied this fate and have measured not only the disappearance of VX from these soils but also the appearance of degradation products. These products included diisopropylaminoethylthiol (I) and its thioether analog (II).

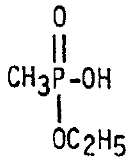


I

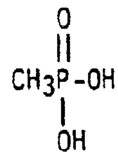


II

The phosphorus-containing degradation products identified in the soils were ethyl hydrogen methylphosphonate (III) and methylphosphonic acid (IV).



III



IV

1.3 Summary

Substantial evidence has been produced to attribute the inability to recover agent from concrete to factors inherent in an interaction between agent and concrete rather than to limitations in solvent extraction techniques or related analytical procedures. This evidence consists of:

- The alkaline, ionic, and hydrated nature of concrete
- The ease with which the agents GB, HD, and VX undergo alkaline hydrolysis (5,6,10)
- Experimental data on soils demonstrating in situ hydrolysis of GB and VX (7,8,11,12,13)
- Documented inability to recover GB, HD, and VX from concrete, even in the absence of any externally applied decontaminant (2,9).

These data suggest that the fate of these agents on concrete is hydrolysis. Experimental data specific to this fate, however, should be derived systematically such that the alternative explanations can be considered.

2.0 OBJECTIVE

The objective of this research project was to identify the fate of the chemical agents GB, HD, and VX on concrete. This study

focused on determining whether the interactions that occur between agent and concrete are physical or chemical. Sufficient evidence existed from independent research efforts as well as previous work on this program to conclude that agent does interact in some unspecified way with concrete and that this interaction prevents or inhibits recovery of agent when it is applied to concrete.

Physical interactions that might account for the inability to readily recover agent include phenomena in which the state of the agent molecule is changed but the molecular composition is unaltered. Examples include adsorption of the agent onto the concrete and adhesion of agent onto interstitial areas within concrete. These processes may be likened to uptake and retention of water by a sponge. Considerable efforts, such as squeezing and heating, are required to completely recover the water from the sponge. However, the water is available to be recovered. By analogy, agent retained in concrete by physical forces would be available for ultimate release to the environment, although considerable effort might be required to cause this release.

Chemical interactions that might account for the inability to recover agent from concrete involve a change in molecular composition of agent, resulting in production of nonagent species. Hydrolysis of agent is a prime example of a chemical reaction likely to occur in concrete, owing to the presence in concrete of reactants associated with traditional methods of bringing about agent hydrolysis. These species include the waters of hydration that are characteristic of the inorganic species that constitute concrete, (e.g. hydrated calcium aluminosilicates) and a potentially effective agent decontaminant. In the event chemical reactions between agent and concrete do occur, then the success of efforts to recover agent will be limited by the speed and extent of these reactions and the extent to which these reactions are reversible. An excellent analogy exists with the decontamination towelettes of the M258 A1 Personnel Decontamination Kit. These towelettes have been impregnated with active decontaminants for either nerve agents (Packet I) or vesicants (Packet II), so that as agent is drawn up into the towelette, the decontaminants react to neutralize the agent. Agent

cannot be recovered from a used towelette unless all the decontaminating ability of the towelette has been spent. If agent were decontaminated in situ by concrete, then recovery of agent can take place only to the extent to which this decontamination reaction has failed to occur.

3.0 APPROACH

Investigation of the fate of agent on concrete involved three major subtasks: Literature Survey; Pulverized Concrete Studies; and Intact Concrete Coupon Experiments. The literature survey provided information that aided interpretation of experimental results. Pulverized concrete was used to determine whether the interaction between agent and concrete is physical or chemical. Intact concrete coupon experiments were conducted to provide a baseline for agent release from concrete into the atmosphere, to extend the information base derived from pulverized concrete studies to include results more nearly approximating field conditions rather than the laboratory environment, and to gain data on agent interactions with concrete that would allow the kinetics of any reaction to be derived.

Specific details on the intended experimental approach were provided in a test plan. Essential details to this experimental approach are summarized below. Actual data is given in Battelle Laboratory Record Book Nos. 38958, 39064 and 39546.

3.1 Literature Survey (Subtask A)

The existing computerized files prepared under Phase I of the Novel Processing Technology Program were examined, along with additional reports identified during analytical method development activities on this Program. The literature survey focused on extracting data from relevant reports to be used during interpretation of project experimental results or during planning of precise experimental procedures. Results from this survey were incorporated, in part, into Section 1.2 of this report.

3.2 Pulverized Concrete Studies (Subtask B)

Subtask B involved the use of dilute agent on pulverized concrete to gather information on the rate, degree and nature of the interaction between the agents and concrete. Diluted agent and pulverized cured concrete was used in this subtask to minimize diffusion-limited phenomena such as the wicking effect observed for concrete dosed with neat agent. The cured concrete was pulverized and sieved to a size not greater than 600 microns.

Three distinct approaches were used in Subtask B. Initially, the influence of both agent concentration and time of contact between agent and pulverized concrete were investigated for a constant mass of concrete and at a single, constant temperature. This effort, referred to as Subtask B.1, allowed planning of a second set of experiments (Subtask B.2), in which the influence of temperature for known and constant contact time and agent concentration was determined. In Subtask B-3 the influence of time of contact between VX and pulverized concrete was investigated with a constant mass of concrete and at a single, constant temperature. Experimental details and discussion of experimental results are given in Section 4.1 of this report.

3.3 Intact Concrete Experiments (Subtask C)

Subtask C involved attempts to extract agent from intact spiked concrete coupons either by thermal desorption or by solvent extraction. The intact cured concrete coupons were of the same dimensions as those coupons used throughout the Novel Processing Technology Program engineering studies*. Results from Subtask B studies were used to provide specific guidance for contact time, agent level for neat agent dosing, and other important experimental details. These details are discussed in Section 4.2, along with the rationale for selection.

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* See Appendix III and V of the main report.

Because intact coupons were used in this work, baseline thermal desorption experiments were conducted to evaluate the effect of heating concrete specimens to 60 C (140 F). These specimens were contaminated separately with each of the three chemical agents at selected contamination densities. The intact coupon was placed in a chamber which was then heated to 60 C. Air, also heated to 60 C, was directed through the chamber and then passed through an atmospheric sampling device (impinger-style bubbler). Analyses of the bubbler solutions were used for evaluating the extent to which agent was volatilized from the intact concrete.

In addition to the thermal desorption experiments, various solvents and solvent contact times were evaluated for extraction of HD from intact concrete.

4.0 EXPERIMENTAL PROCEDURES AND RESULTS

4.1 Pulverized Concrete Studies (Subtask B)

4.1.1 Influence of Concentration and Time (Subtask B.1)

4.1.1.1 Experimental Procedures. The influence of agent concentration and contact time were examined by adding a known mass of pulverized concrete to the desired concentration of agent in hexane and removing an aliquot for residual agent analysis at selected times after addition of concrete. Contact time refers to the time between addition of the pulverized concrete and withdrawal of the aliquot for residual agent analysis. Analysis was conducted by capillary column gas chromatography, equipped with a flame photometric detector (GC/FPD) operating in the phosphorus mode for GB and VX and the sulfur mode for HD.

Solution concentrations of agent selected for the pulverized concrete experiments were 13, 52, 104, and 520 mg/L; which correspond to agent-to-concrete ratios of 0.045, 0.18, 0.36, and 1.8 mg/g, based on 100 mL solutions and 28 g pulverized concrete. These ratios correspond

to agent surface coverages of 1.2, 4.8, 9.6, and 48 g-agent per m^2. The basis for these ratios is detailed below for 0.045 mg/g:

Dimensions of concrete coupon = 5 in. x 5 in. x 0.25 in.
Spiked area of coupon = $(4\ \text{in.})^2/4 = 12.6\ \text{in}^2 = 81.1\ \text{cm}^2$
Target agent coverage = 10 mg agent/81.1 cm^2 = 0.12 mg/cm^2
= 1.2 g/m^2*
Average mass of 5x5 x 0.25 inch coupon = 225 g (range = 200-250 g)
Mass of agent per coupon = (0.11 mg/cm^2 x 81.1 cm^2 = 10 mg
Ratio of agent : concrete = $\frac{10\ \text{mg}}{225\ \text{g}}$ = 0.045 mg-agent/g-concrete.

Contact times of 0 (that is, immediately prior to addition of concrete), 30, 60, 120, and 1440 minutes were used. All experiments were conducted in 250 ml Erlenmeyer flasks that were immersed in a temperature bath maintained at 25 C. The pulverized concrete was maintained in slurry by vigorous mechanical mixing. Each experiment was conducted in duplicate and was analyzed singly via GC/FPD. A method control containing agent but no pulverized concrete was carried along with each experiment. Results from this method control were used to estimate loss of agent or solvent during the experiment. In addition, a method blank of pulverized concrete in hexane was analyzed to ensure no artifacts were present to interfere with the analytical scheme. Examination of the results from this work showed that the studies involving HD required a more prolonged total contact time to obtain useful data. Consequently, additional work was done using a single concentration of HD (104 mg/L or a ratio of 0.36 mg-agent/g-concrete) and contact times of 360, 2070, 4320, and 4710 min (0.25, 1.44, 3.00, and 3.27 days).

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* This coverage was used in previous decontamination tests (see Appendix V of the main report).

4.1.1.2 Experimental Results. Experimental results are summarized in Table 3. These results are expressed in terms of percent of the original agent remaining at each sampling interval. This means of expressing results facilitates comparison of results among agent concentrations. Values in Table 3 which are greater than 100 percent agent remaining may indicate that hexane evaporation, in excess to that of any agent evaporative losses, had occurred. Evaporative loss of solvent would tend to increase the concentration of agent in solution which would be reflected in an apparent increase in percent agent remaining. Subsequent decreases in the percent agent remaining may be due either to evaporation of more agent than solvent or to degradation by, for example, hydrolysis from absorption of water vapor from the atmosphere.

As shown by the data in Table 3, addition of concrete resulted in disappearance of agent from solution. This disappearance is most dramatic for agent GB, where disappearance appears to reach a constant level of less than one percent remaining within 30 minutes, the first sampling interval past addition of concrete. Disappearance of agent VX follows a similar profile but displays greater sensitivity to both initial concentration and contact time. Agent HD appears to disappear; however, this disappearance is substantially slower and less pronounced at higher initial concentrations than observed in the GB and VX experiments.

Because of the relatively slow rate of HD disappearance, several experiments were conducted utilizing longer contact times. Results from these studies, presented in Table 4, were analyzed assuming that the disappearance of HD is a first-order chemical reaction. This assumption seems valid because of the excellent correspondence among the calculated rate constants (see Table 4). The average first order rate constant is 2.86×10^{-4} min, which corresponds to a half-life of 2420 min (approximately 40 hours). These results seem indicative of a chemical reaction occurring between concrete and HD.

Experiments in Subtask B.1 demonstrated conclusively that concrete influences the disappearance of the chemical agents GB, HD, and VX.

TABLE 3. PULVERIZED CONCRETE EXPERIMENTAL RESULTS FOR INFLUENCE OF AGENT CONCENTRATION ON RATE OF DISAPPEARANCE (TEMPERATURE = 20 C)

Agent	Initial Ratio Agent-to-Concrete (mg/g)	Percent Agent Remaining After Addition of Concrete Time (minutes)(a) 30	60	120	1440
GB	No concrete	94.7	96.2	89.7	79.0
	0.045	1.2	0.8	1.1	1.9
	No concrete	89.7	89.6	90.1	89.2
	0.18	1.0	0.6	1.1	1.1
	No concrete	99.4	94.6	94.3	86.3
	0.36	0.9	0.9	0.8	2.1
	No concrete	94.1	98.2	129(b)	134(b)
	1.8	0.8	<0.1	<0.1	<0.1
HD	No concrete	98.3	81.7	92.6	82.2
	0.045	90.6	86.6	86.0	62.4
	No concrete	100.5	100.5	100.3	100.3
	0.18	97.7	95.8	90.3	44.3
	No concrete	99.6	99.5	99.8	99.7
	0.36	99.8	98.3	93.3	83.7
	No concrete	110(b)	102.3(b)	97.1	98.0
	1.8	102.7(b)	94.4	94.6	85.4
VX	No concrete	103.0(b)	100.3	78.9	78.4
	0.045	3.4	<1.0	1.8	<1.0
	No concrete	108(b)	118(b)	121(b)	123(b)
	0.18	3.3	4.4	3.9	4.0
	No concrete	103.6(b)	111(b)	113(b)	116(b)
	0.36	2.8	1.9	1.8	1.7
	No concrete	93.0	89.8	88.4	75.4
	1.8	23.3	12.5	6.5	<1.0

(a) Results reported for all samples containing concrete are the average of duplicate runs. For values where one run was below the method detection limit, a value of 0 percent was used in calculating the average.

(b) Results of greater than 100 percent agent remaining may indicate loss of solvent (hexane).

TABLE 4. DISAPPEARANCE OF HD ON EXPOSURE TO PULVERIZED CONCRETE

Min.	HD Remaining mg/L	%	k,[a] $min.^{-1}$
0	104[b]	100	-
360	93.7	90.1	2.93×10^{-4}
2070	57.0	54.8	2.91×10^{-4}
4320	32.2	31.0	2.70×10^{-4}
4710	26.5	25.5	2.90×10^{-4}
		Avg =	$(2.86 \pm 0.11) \times 10^{-4}$

(a) $k = \ln \frac{(HD)_0}{(HD)_t} \times \frac{1}{t}$, for first-order kinetics ($A_t = A_0^{-kt}$) where $(HD)_0$ = concentration at t = 0 (i.e., initial concentration).

(b) Equivalent to 0.36 mg-agent/g-concrete.

4.1.2 Influence of Temperature (Subtask B.2)

4.1.2.1 Experimental Procedures. Results from Subtask B.1 were used to select experimental conditions of contact time and agent concentration to be held constant such that the influence of temperature might be determined. Most experiments during this subtask were conducted according to the following protocol:

(1) A single method control (agent solution without concrete) plus five identical mixtures of agent and concrete were used.

(2) Duplicate samples were withdrawn at contact times of zero minutes and 5 minutes (GB only), 960 minutes (HD only), and 15 minutes (VX only).

(3) Samples were analyzed singly via GC/FPD.

(4) Reaction temperatures were 25, 40, and 55 C.

(5) Results were expressed as percent remaining agent on a comparison basis, with the method control for that same contact time being used for reference as 100 percent remaining.

(6) Evaporative losses of solvent and losses of agent with time were estimated by comparing the time zero samples with the method control for the total contact period.

In response to the experimental results several modifications to the protocol were made. These included evaluation of 1 and 2 minute contact times for GB and evaluation of 0 C reaction temperature for GB and VX.

The rationale for initial selection of the agent concentration, contact time, and reaction temperature is given below for each agent.

4.1.2.1.1 Agent GB. Results from Subtask B.1 suggested that GB disappears quite rapidly at all concentrations studied. Initially, a contact time of 5 minutes was used. An agent concentration of 520 mg/L (ratio of 0.18 mg/g) was selected as a sufficiently high concentration so that te · erature effects might be observed.

4.1.2.1.2 Agent HD. Results from Subtask B.1 suggested that HD disappearance is significantly slower than that of either GB or VX. A contact time of 16 hours (960 minutes) at a concentration of 52 mg/L (ratio of 0.18 mg/g) was selected to allow temperature effects, if any, to be observed. Subtask B.1 results indicated that about 50 percent of the original HD should remain at this combination initial concentration, contact time, and temperature.

4.1.2.1.3 Agent VX. Results from Subtask B.1 suggested that Agent VX disappearance is demonstrably different at the highest concentration than was observed for the three lower concentrations. Therefore, a 520 mg/L concentration was used with a contact time of 15 minutes at 25 C. Based on Subtask B.1 results, this combination of concentration, contact time and temperature should result in approximately 50 percent of the VX to remain.

4.1.2.2 Interpretation of Subtask B.2 Results. In advance of developing experimental results from the investigation of the influence of temperature on agent disappearance, guidance was developed to aid in interpretation of results. This guidance was felt to be especially useful in sorting out the prospect of physical absorption versus chemical reaction as the mechanism for agent disappearance. This guidance is given below.

If Subtask B.2 results from any agent indicate that the percent remaining decreases with increasing temperature, these results would be interpreted as positive indication that the disappearance of agent in the presence of concrete is caused by a chemical reaction. This interpretation would be consistent with the general observation that the rate of a chemical reaction is increased by an increase in temperature. This increase may be attributed to the concomitant increase in collisional energies available to the reactant molecules.

If Subtask B.2 results indicate that the percent remaining increases with increasing temperature, these results would be interpreted as indicative of a physical mechanism for agent

disappearance in the presence of concrete. This interpretation would be consistent with a sorption mechanism, in which agent is sorbed by the concrete. This sorption involves attraction energies collectively known as van der Waals forces. As temperature increases the molecular vibrational energies increase thereby allowing the weaker van der Waals attraction that holds the molecules to the surfaces to be overcome.

4.1.2.3 Experimental Results. Results from Subtask B.2 are summarized in Table 5. These data are strongly indicative that the interaction between agent and concrete is a chemical reaction. For agents GB and VX, solid evidence was obtained by the decrease in percent agent remaining as temperature was increased. For example, the data in Table 5 show the percent remaining for GB with a 2-minute contact time decreased steadily from 76.0 percent to 6.3 percent as the temperature increased from 0 to 55 C. Results for GB with a 5-minute exposure time demonstrated complete loss of agent. Results for GB with a 1-minute contact time were anomalous, most likely due to incomplete mixing during the extremely brief contact time.

Results for VX between 25 and 55 C show a similar pattern of steady decrease, from 19.1 to 12.5 to 9.0 percent remaining. The low result for VX remaining at 0 C (5.5 percent) may be attributed to the complete miscibility of VX in water at temperatures below the lower consolute temperature of 9.4 C. This enhanced solubility may in turn enhance any hydrolytic activity of VX.

Results for HD were less conclusive than they were for GB and VX. Although the percent remaining decreases in going from 25 to 40 C, it rose in going to 55 C. Therefore, interpretation of results is less straightforward in that disappearance of HD may be a combination of both a physical adsorption and a chemical reaction mechanism.

4.1.3 Kinetics of the Interaction of VX with Pulverized Concrete (Subtask B-3)

4.1.3.1 Experimental Procedures. Previous results from Subtask B were used to select the contact times and agent concentration

TABLE 5. EFFECT OF TEMPERATURE ON DISAPPEARANCE OF AGENT EXPOSED TO PULVERIZED CONCRETE

Agent	Initial Concentration, mg/L	Contact Time, min.	Temperature, C	HD Remaining, Percent
GB	520	5	25	<1 (BDL)[(a)]
			40	<1 (BDL)
			55	<1 (BDL)
GB	520	2	0	76.0
			25	49.3
			55	6.3
GB	520	1	0	31.5
			25	46.1
			40	22.0
			55	22.9
HD	52	960	25	88.6
			40	33.3
			55	47.2
VX	520	15	0	5.5
			25	19.1
			40	12.5
			55	9.0

(a) BDL = Below detection limit.

for examination of the kinetics of VX disappearance versus decomposition product formation. All experiments were conducted according to the following protocol:

(1) A single agent control (agent solution without concrete), a single interference control (concrete solution without agent), plus three identical mixtures of agent and concrete were used. A spike level of 0.02 mg VX/g concrete was used.

(2) Duplicate samples were withdrawn at contact times of 0 minutes, 180 minutes, 420 minutes, and 1440 minutes.

(3) Samples were analyzed singly via GC/FPD and GC/FID.

(4) Reaction temperature was 25 C.

(5) Results were expressed as percent agent remaining on a comparison basis, with the method control for that same contact time being used for reference as 100 percent remaining.

(6) Evaporative losses of solvent and losses of agent with time were estimated by comparing the time zero samples with the method control for the total contact period.

4.1.3.2 Experimental Results. The results from the kinetic study are summarized in Table 6. This data again suggests that the interaction between agent and concrete is a chemical reaction. Example chromatograms showing loss of VX and formation of a possible degradation product with time given in Figures 3 through 7.

4.1.4. Examination of Selected Samples by Gas Chromatography/Mass Spectrometry

4.1.4.1 Experimental Procedure. Selected samples from pulverized concrete experiments were analyzed by gas chromatography/mass

TABLE 6. RESULTS OF VX KINETICS WITH CONCRETE

Agent/Sample Matrix	Dose Level[(a)], mg agent/g concrete	Contact Time, min	Agent[(b)] in solution, percent
VX/hexane	.02	0	100
None/hexane	.02	0	0
VX/concrete/hexane	.02	0	100
VX/concrete/hexane	.02	0	100
VX/concrete/hexane	.02	0	100
VX/hexane	.02	180	115
None/hexane	.02	180	0
VX/concrete/hexane	.02	180	3
VX/concrete/hexane	.02	180	0
VX/concrete/hexane	.02	180	0
VX/hexane	.02	420	119
None/hexane	.02	420	0
VX/concrete/hexane	.02	420	0
VX/concrete/hexane	.02	420	0
VX/concrete/hexane	.02	420	0
VX/hexane	.02	1440	107
None/hexane	.02	1440	0
VX/concrete/hexane	.02	1440	0
VX/concrete/hexane	.02	1440	0
VX/concrete/hexane	.02	1440	0

(a) The pulverized concrete samples weighed 28 grams.
(b) Compared to 0 minute exposure.

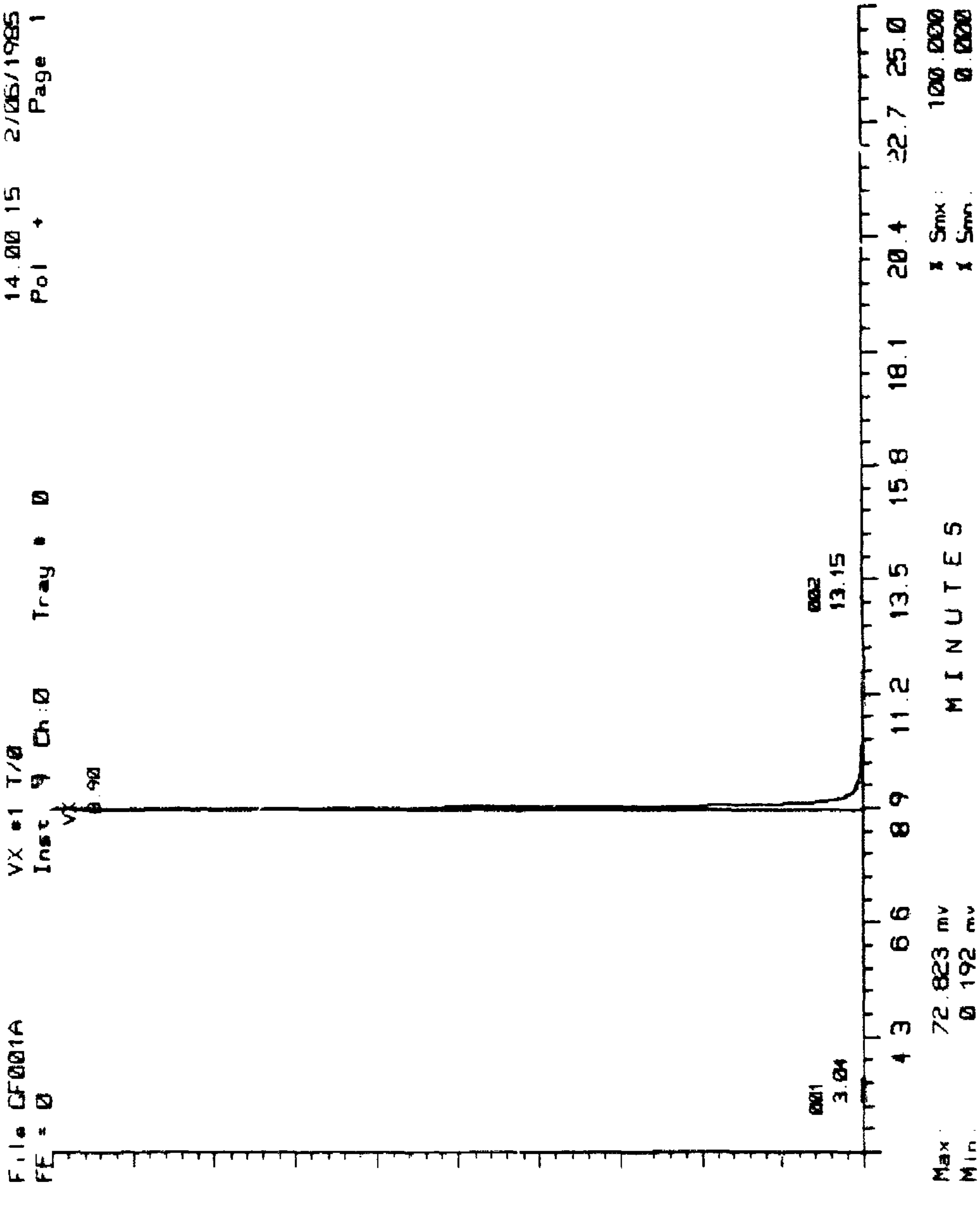


FIGURE 3. GAS CHROMATOGRAM OF VX/CONCRETE/HEXANE SAMPLE AFTER 0 MINUTES EXPOSURE

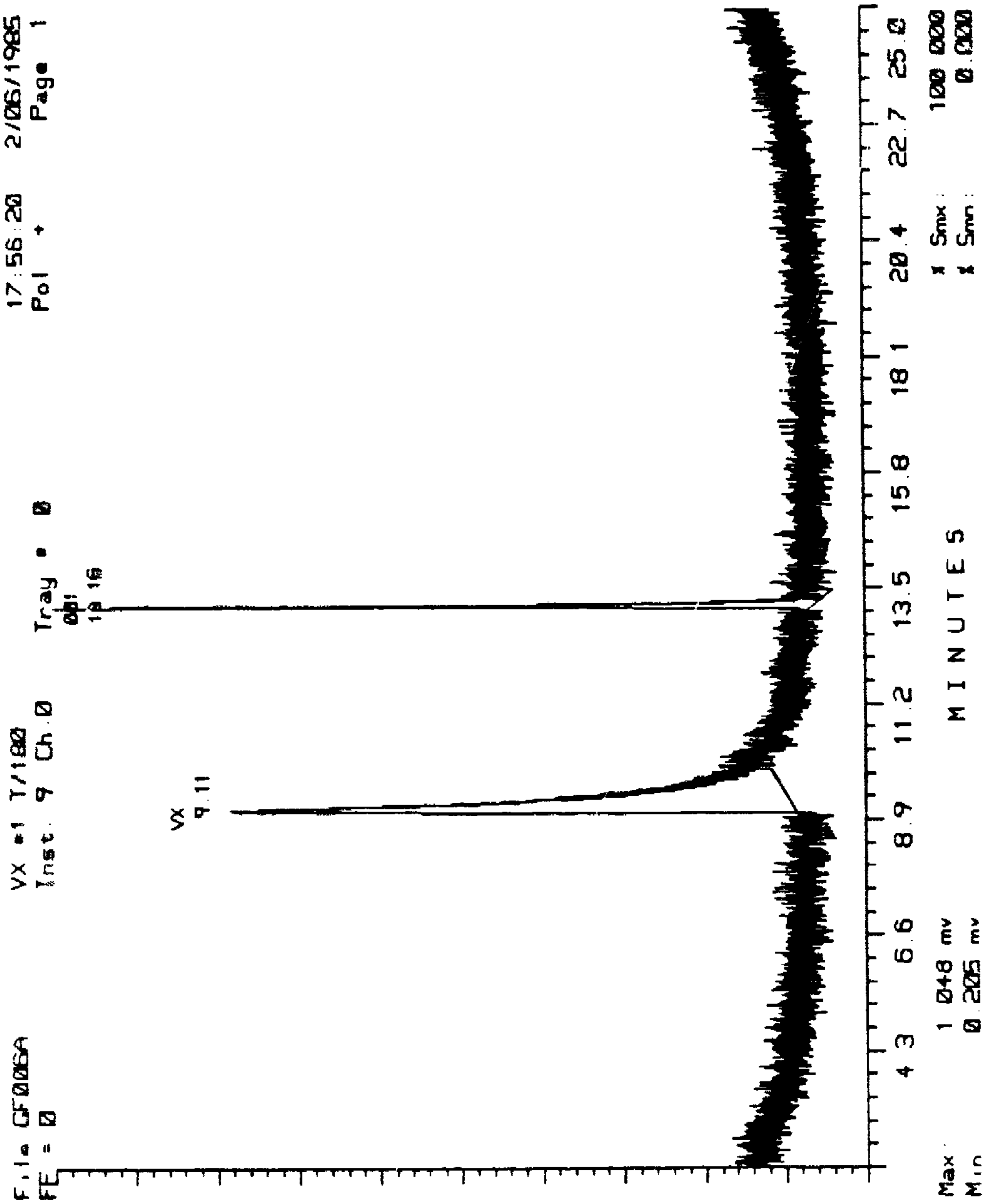


FIGURE 4. GAS CHROMATOGRAM OF VX/CONCRETE/HEXANE SAMPLE AFTER 180 MINUTES EXPOSURE

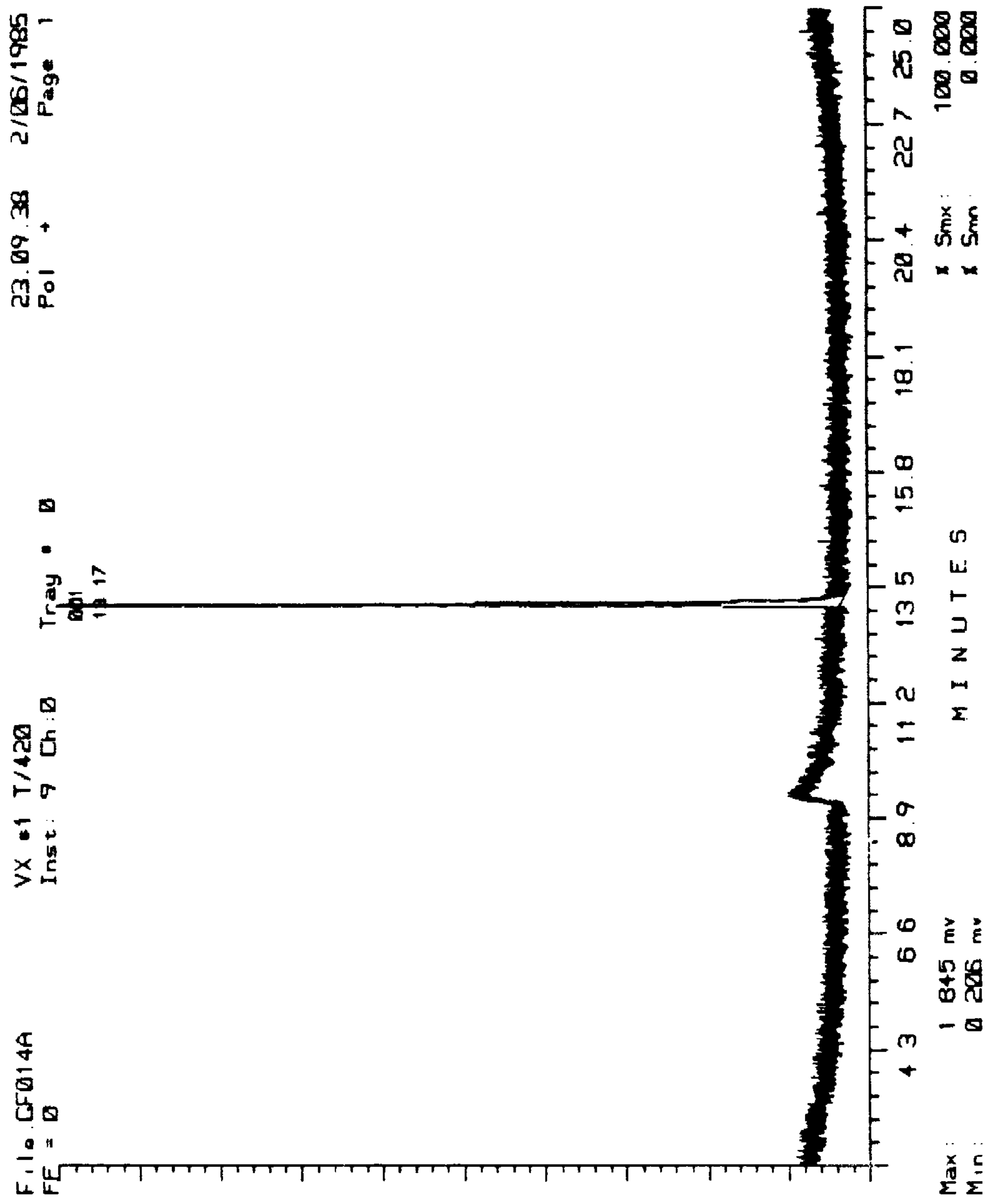


FIGURE 5. GAS CHROMATOGRAM OF VX/CONCRETE/HEXANE SAMPLE AFTER 420 MINUTES EXPOSURE

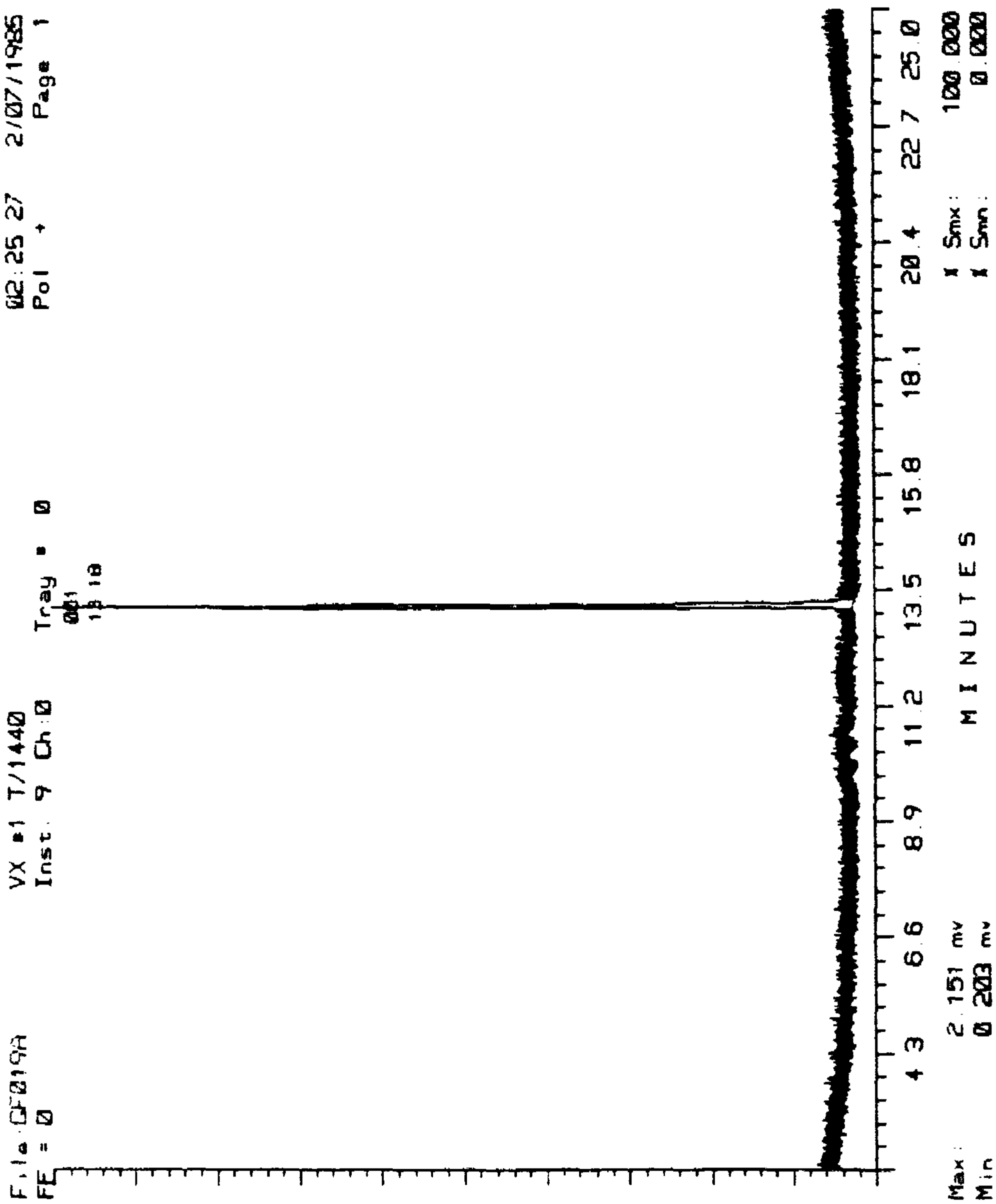


FIGURE 6. GAS CHROMATOGRAM OF VX/CONCRETE/HEXANE SAMPLE AFTER 1440 MINUTES EXPOSURE

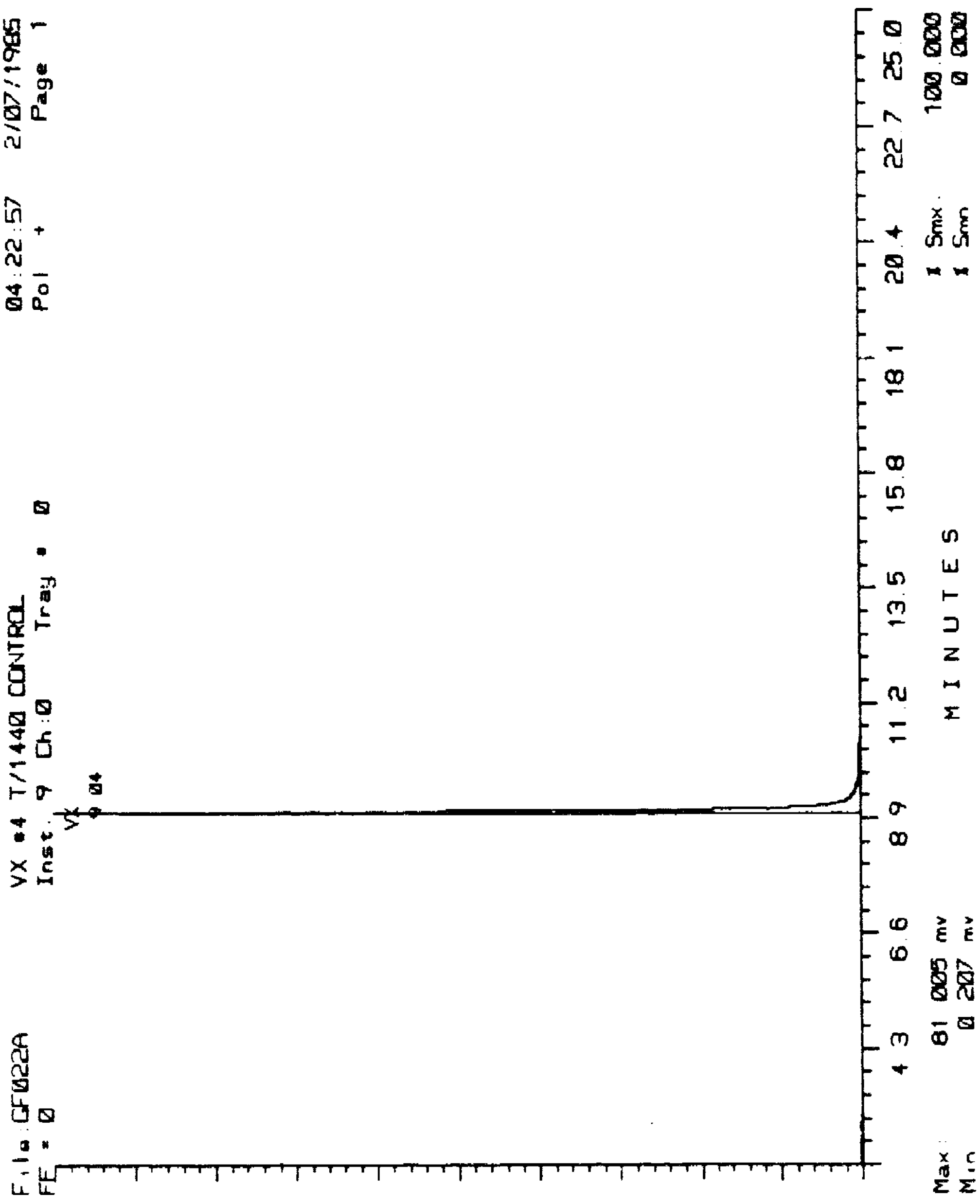
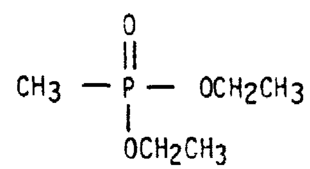


FIGURE 7. GAS CHROMATOGRAM OF VX/HEXANE CONTROL SAMPLE AFTER 1440 MINUTES EXPOSURE

spectrometry (GC/MS). The GC/MS examination was directed toward identification of potential degradation products. Comparison with control samples (agent that was not exposed to concrete but was treated similarly) provided a positive means of ensuring that the degradation products were due to the presence of pulverized concrete.

4.1.4.2 Experimental Results. GC/MS analysis of a sample from a VX/pulverized concrete experiment produced positive identification of diethyl methyl phosphonate (DEMP):



Diethyl Methyl Phosphonate (DEMP)

DEMP was not present in the control samples. Furthermore, DEMP was also confirmed in the chemical concept evaluations* samples for use of steam as a decontaminant. The mass spectrum from which DEMP was identified is given in Figure 8.

Similar examination of GB and HD samples failed to uncover any agent degradation products in the GC/MS analyses. Although these results were disappointing in view of the other evidence for a chemical reaction, inability to detect any degradation products was not surprising due to the extremely low levels of such products in the final sample matrix.

4.2. Intact Concrete Experiments (Subtask C)

4.2.1. Vapor Sampling of Intact Concrete

4.2.1.1. Experimental Procedures.** Intact 1/4-inch thick concrete coupons were dosed with neat agent in accordance with an approved

* See Appendix II of the main report.
** A detailed description of the vapor sampling apparatus is given in Appendix V of the main report.

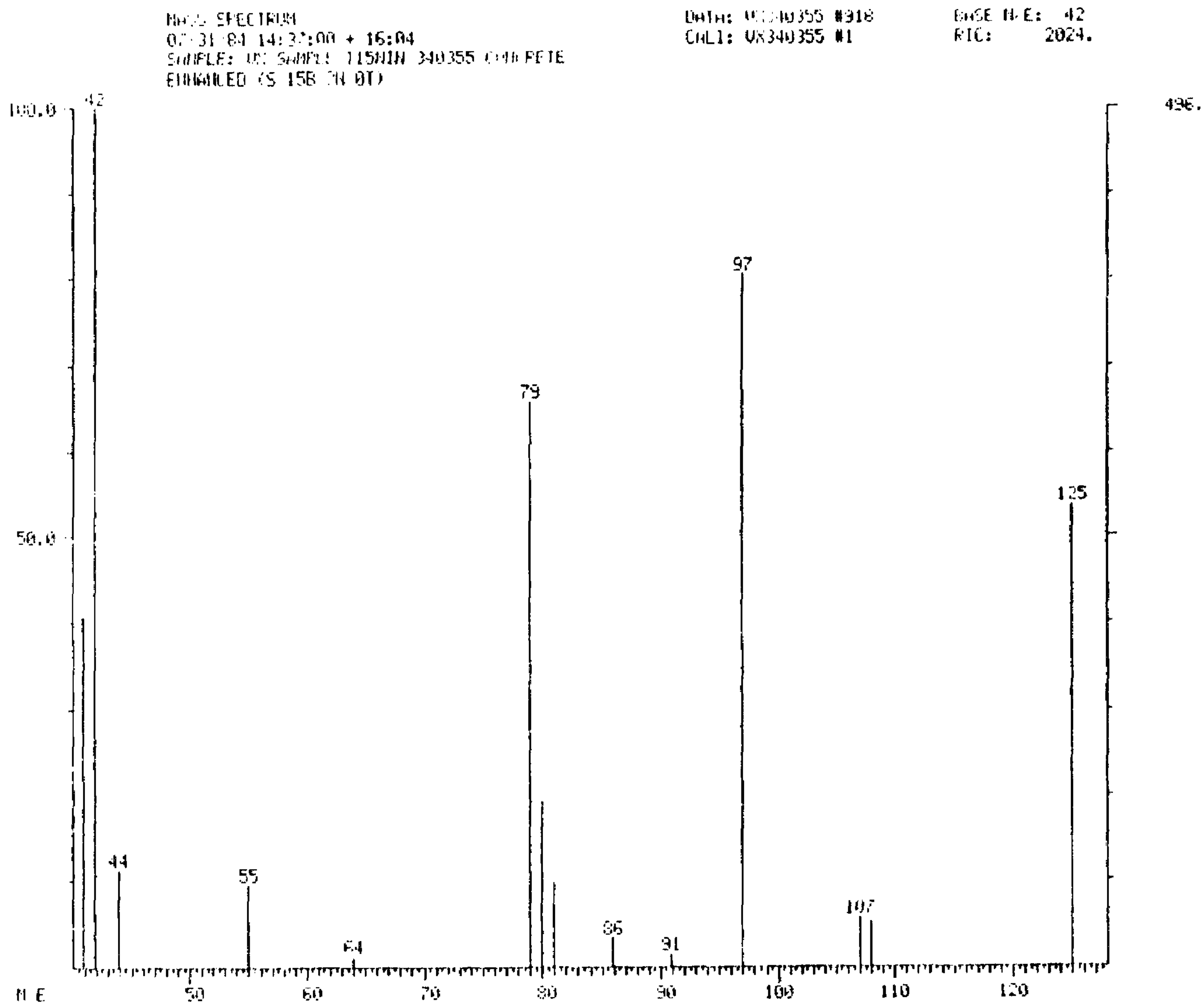


FIGURE 8. MASS SPECTRUM OF A VX/PULVERIZED CONCRETE SAMPLE FROM WHICH DIETHYL METHYL PHOSPHONATE (DEMP) WAS IDENTIFIED

Standard Operating Procedure for Handling Chemical Surety Material. The dosing level was either 0.045 mg agent/g concrete or 1.8 mg agent/g concrete. The spiked coupon was then allowed to stand in an enclosed chamber for 10 minutes (GB), 120 minutes (VX, or 1440 minutes (HD). These times were based on pulverized concrete data for nearly complete removal of agent from solution. After standing for the required period of time, the coupon was placed in a vapor sampling apparatus which was then heated to 60 C (140 F). Heated air at 60 C was directed through the apparatus and into an impinger train to collect any volatilized agent. In addition to spiked coupons, blanks (i.e., no agent present) were tested to determine if vapor sampling concrete would affect the analytical procedure. The air stream was sampled using impinger-style bubblers, which were analyzed by enzymatic assay method for volatilized nerve agent and gas chromatography/ Hall electrolytic detector for HD.

Following cessation of vapor sampling, the dosed coupon was returned to its container. The coupon was broken apart mechanically to enhance wettability and to make the coupon more amenable to subsequent work-up. The concrete was transferred to a large vessel and allowed to soak in approximately 500 mL methylene chloride. An aliquot (100 mL) was removed after 16-24 hours of contact with the concrete, and then reduced to a final volume of approximately one mL. This concentrated extract was analyzed via GC/MS for agent and agent degradation products.

4.2.1.2. Experimental Results. Results of the intact coupon vapor sampling experiments are summarized in Table 7. The following fundamental points arise from these results:

TABLE 7. RESULTS OF INTACT CONCRETE VAPOR SAMPLING

Agent	Dose Level[a] mg agent/ g Concrete	Neat Agent Spiked (mg)	Agent Found in Impinger (mg)	Agent Concentration[b] in Air (mg/m^3)
Blank (HD)[c]	0	0	<0.0002	<0.002
HD	0.045	9.5	<0.0002	<0.002
HD	1.8	378.5	<0.0002	<0.002
Blank (GB)[c]	0	0	0.048	0.400
GB	0.045	9.5	0.0022	0.018
GB	1.8	371.5	0.0023	0.019
Blank (VX)[c]	0	0	0.0007	0.006
VX	0.045	9.4	0.0040	0.033
VX	1.8	373.3	0.0040	0.033

(a) The intact concrete coupon weighed from 206.4 to 212.1 gms.
(b) Agent Concentration = Agent found in impingers from first sampling period (mg) divided by the volume of air sampled.
(c) An unspiked concrete coupon was subjected to the vapor sampling treatment. The impingers were then analyzed for the respective agent.

- HD was not detected in any impinger sample.
- Vapor sampling of unspiked concrete caused interferences to GB and VX determination by the enzymatic procedure. The interference may be due to entrained concrete dust in the sampling air stream.
- The enzymatic analyzer showed positive responses when sampling GB or VX contaminated coupons although the magnitude of the response was independent of the dose level. This suggests that the response may have been due to the concrete rather than the presence of GB or VX.

Based on these results, no evidence of agent volatilization at 60 C was seen. Furthermore, the lack of specificity inherent in the enzymatic assay for nerve agents allows false positives to mask genuine agent volatilization, if it should occur. The enzymatic method cannot be recommended for use in concrete structures, as the results in Table 5 demonstrate.

The GC/MS analyses failed to produce any evidence of either agent or agent degradation products in the concrete coupon extracts.

4.2.2. HD Recovery from Intact Concrete

Results of the agent/concrete experiments indicated that GB and VX rapidly interact with concrete. This would lead to ambiguity in interpreting the results of subsequent concrete decontamination experiments because the effect of the decontamination treatment on the nerve agent may be indistinguishable from the effect of the concrete. As such, an inert material (i.e., unglazed porcelain) was selected in place of concrete for the GB and VX decontamination test.*

In contrast to GB and VX, significant amounts of HD were extractable following contact times similar to the duration of

* See Appendix V of the main report.

decontamination treatments. As such, further effects were performed to quantify the extractability of HD from concrete as a function of contact time and solvent type.

4.2.2.1 Experimental Procedures. Intact 1/4-in. thick concrete coupons were dosed with neat agent in accordance with an approved Standard Operating Proecdure for Handling Chemical Surety Material. The dosing level was 1.8 mg/g concrete. The spiked coupon was then immediately extracted or allowed to stand in an enclosed chamber for 1440 minutes. The time of 1440 minutes was chosen as the longest period a coupon would be exposed for decontamination testing. After standing for the required period of time, the coupon was crushed and extracted. The crushing process reduced the size of the concrete to pieces each less than 1/2-in. This was confirmed by passing the material through a $\mathbf{\overline{\$}}$ 24/40 ground glass joint. The extraction solvent was either 150 ml of hexane or methylene chloride. The solvent extracts were then analyzed by Gas Chromatograph/Electrolytic Conductivity Detector (Hall).

4.2.2.2 Experimental Results. Results of the HD recovery from intact concrete experiments are summarized in Table 8. The following fundamental points arise from these results:

- Greater than one percent of the initial HD was detected in the sample after a contact time of 1440 minutes.
- Assuming an HD recovery of one percent, a 99.99 percent decontamination efficiency could be observed in subsequent decontamination tests. The decontamination efficiency is calculated as follows:

Decontamination Efficiency (%) = 100 x $\{$1-GC Detection Limit (mg/mL) $\div$ [Spiking Level (mg HD) X Recovery Efficiency $\div$ Final Volume of Extract Following Concentration (ml)]$\}$

$= 100 \times \{1 - 0.0001 \text{ mg/ml} \div [378 \text{ mg} \times 0.01 \div 2 \text{ ml}]\}$

$= 99.99\%$

Based on the HD recovery data, it was recommended that the HD/concrete decontamination tests be conducted. Other recommendations included the use of

- The extraction procedure outlined in Section 4.2.2.1
- A dose level of 1.8 gm HD/gm concrete
- A maximum 24 hours contact period between spiking the fresh coupons and extracting the decontaminated coupons.

TABLE 8. RESULTS OF INTACT CONCRETE SOLVENT EXTRACTIONS

Agent	Solvent	Dose Level[(a)] mg Agent/g Concrete	Neat Agent Spiked (mg)	Exposure Time[(b)] (min)	Percent Agent in Extract
HD	Hexane	1.8	378	0	30
HD	Hexane	1.8	378	0	22
HD	Hexane	1.8	378	0	33
HD	Hexane	1.8	378	1440	.75
HD	Hexane	1.8	378	1440	.10
HD	Hexane	1.8	378	1440	1.45
HD	Methylene Chloride	1.8	378	0	57
HD	Methylene Chloride	1.8	378	0	59
HD	Methylene Chloride	1.8	378	0	60
HD	Methylene Chloride	1.8	378	1440	12
HD	Methylene Chloride	1.8	378	1440	2.0
HD	Methylene Chloride	1.8	378	1440	1.0

(a) The intact concrete coupon weighed from 208 to 230 grams with an average of 215.6 grams for ten coupons.

(b) The exposure time does not include the estimated 10 minutes required to crush coupons.

5.0 CONCLUSIONS/RECOMMENDATIONS

The inability to quantitatively extract GB, VX and HD following spiking onto concrete has been experimentally demonstrated to be caused by an interaction between the agent and concrete. Pulverized and intact concrete studies suggest that the interaction is a chemical reaction.

A summary of the results from the pulverized concrete test is given by agent as follows.

GB

- GB disappears from solution in contact with pulverized concrete for a period as short as five minutes.
- The rate of GB disappearance is not dependent on the agent concentration within the limits investigated.
- For a two minute contact time, the rate of GB disappearance from solution increases with an increase in temperature. This suggests that the interaction of GB with concrete is a chemical reaction.
- GC/MS analyses failed to identify GB degradation products.

VX

- VX disappears from solution in contact with pulverized concrete for a period as short as 30 minutes.
- The rate of VX disappearance is sensitive to the initial agent concentration. The initial rate of VX disappearance is substantially slower for a high initial VX concentration (1.8 mg-VX/g-concrete) than for lower initial VX concentrations (0.36 mg-VX/g-concrete or lower).
- The rate of VX disappearance from solution increases with an increase in temperature between 25 and 55 C. This suggests that the interaction of VX with concrete is a chemical reaction.
- GC/MS analyses identified DEMP (diethyl methyl phosphonate) in a sample from the pulverized concrete experiments. DEMP was previously shown to be a VX degradation product from steam decontamination.

HD

- Residual HD remains in solution which is in contact with pulverized concrete for a period as long as 78 hours.

- The rate of HD disappearance is sensitive to initial concentration and appears to follow first-order kinetics. The half-life of HD in contact with pulverized concrete at 25 C is about 40 hours.

- Inconclusive results was obtained on the temperature effects on HD disappearance.

- GC/MS analyses failed to identify HD degradation products.

A summary of the results of the intact concrete coupon tests is given as follows:

- Vapor sampling of unspiked concrete coupons caused interferences to the enzymatic analytical method for GB and VX. The interference may be due to entrained concrete dust in the sampling air stream. No interferences were observed for analysis of HD by the GC/Hall detector techniques.

- Vapor sampling of intact concrete coupons which were contaminated with GB and then heated to 60 C showed positive responses from GB. However, the magnitude of the responses were less than that obtained when vapor sampling unspiked concrete coupons.

- Vapors sampling of intact concrete coupons which were contaminated with VX and then heated to 60 C showed positive responses for VX. Although the magnitude of the responses was greater than that obtained when vapor sampling unspiked concrete coupons, the magnitude of the responses were independent of the agent dose level.

- Vapor sampling of intact concrete coupons which were contaminated with HD and then heated to 60 C did not show any positive responses for HD.

- Sampling and analytical procedures were developed for the recovery of HD from intact concrete coupons.

The data from the fate-of-agent in concrete experiments suggests that the decontamination of concrete from field structures and facilities used to manufacture/handle CW agents, especially in the case of GB, may not be required. The use of agent protective and agent impermeable paints in future agent facilities, especially those handling

nerve agents, should be reconsidered. Further efforts are required to conclusively prove that the interaction between agents and concrete is a chemical reaction through identification of agent degradation products.

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APPENDIX VIII

SUBTASK 10. JACADS DECONTAMINANT DATA BASE

TASK 3, SUBTASK 10

TEST REPORT

ON THE

EVALUATION OF CANDIDATE JACADS DECONTAMINANTS

Contract No. DAAK11-81-C-0101

to

UNITED STATES ARMY
TOXIC AND HAZARDOUS MATERIALS AGENCY

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EXECUTIVE SUMMARY

This experimental study evaluated the ability of three candidate chemical decontaminants to decontaminate specific unpainted and painted steel surfaces representative of construction materials selected for the JACADS design. Decontamination solutions of 10% Na_2CO_3 and 1% NaOH were separately tested to decontaminate steel coupons spiked with GB. A 5% (off-the-shelf) NaOCl solution was tested to decontaminate VX and HD. Five inch square coupons of unpainted 316L stainless steel, unpainted galvanized steel, Epoliod G series painted galvanized steel, and Plasite 7122 painted galvanized steel were spiked with 10 mg of agent and spray decontaminated with one of the aqueous solutions.

Following decontamination, the coupons, spent decontamination solution and chamber rinses were analyzed for residual agent. Results suggest that the JACADS decontaminants are effective in that the coupons were decontaminated to either below the detectable limit or to low levels of residual agent.

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TO
UNITED STATES ARMY
TOXIC AND HAZARDOUS MATERIALS AGENCY

1.0 INTRODUCTION

Current Johnston Atoll Chemical Agent Demilitarization System (JACADS) planning envisions using 5 percent aqueous sodium hypochlorite solution (NaOCl - household bleach) as a decontaminant for HD and VX, and either a 10 percent aqueous sodium carbonate solution or a one percent sodium hydroxide solution as a decontaminant for GB. These solutions would be used for decontamination of the following matrices: (1) major spills, (2) painted concrete surfaces, (3) steel surfaces, and (4) Demilitarization Protective Ensemble (DPE) suit material. A previous literature review* performed by BCL[1] indicated that knowledge gaps exist in the data base pertaining to the adequacy of:

- decontamination of wetted painted concrete and DPE smears contaminated with either HD or VX using NaOCl bleach,
- decontamination of DPE smears, wetted steel or wetted painted concrete contaminated with GB using 10 percent sodium carbonate,
- decontamination of wetted steel contaminated with HD using 5 percent NaOCl,

* See Appendix A

- correlating agent decomposition data obtained in vessel (i.e., beakers, tanks, etc. in which agitation was employed) experiments with conditions encountered when decontaminating a major spill.

This study addresses knowledge gaps pertaining to wetted steel and wetted painted steel contaminated with either GB, VX or HD. Data pertaining to the decontamination of DPE smears is given in Government test reports.[2]

2.0 OBJECTIVE

The objective of this experimental study was to evaluate the following decontaminants:

- 5 percent sodium hypochlorite solution in water (NaOCl) for HD and VX
- 1 percent sodium hydroxide solution in water (NaOH) for GB
- 10 percent sodium carbonate solution in water (Na_2CO_3) for GB.

These decontaminants were evaluated by spray application of the decontaminant solution to agent contaminated test coupons. A matrix showing the decontaminants versus test coupon type, is given in Table 1.

3.0 MATERIALS

3.1 Agents

Munition grade GB, VX and HD were used in the tests instead of SARM's because chemical stabilizers make them more difficult to decontaminate. Also, munition grade agents are more representative of the type of agent contamination that will be encountered in the JACADS facility.

TABLE 1. JACADS DECONTAMINATION TESTS

Decontaminant	Agent	Test Coupon	Paint
5 percent NaOCl	HD	Galvanized Steel	None
		Galvanized Steel	Epoloid 5-G5[a]
		Galvanized Steel	PPC No. 7122[b]
		316L Stainless Steel	None
5 percent NaOCl	VX	Galvanized Steel	None
		Galvanized Steel	Epoloid 5-G5
		Galvanized Steel	PPC No. 7122
		316 L Stainless Steel	None
10 percent Na_2CO_3	GB	Galvanized Steel	None
		Galvanized Steel	Epoloid 5-G5
		Galvanized Steel	PPC No. 7122
		316 L Stainless Steel	None
1 percent NaOH	GB	Galvanized Steel	None
		Galvanized Steel	Epoloid 5-G5
		Galvanized Steel	PPC No. 7122
		316L Stainless Steel	None

(a) Supplied by Rowe Products.

(b) Plastic Protective Coating No. 7122 supplied by Wisconsin Protective Coating.

3.2 Coupons

Test coupons were prepared from stock 22 gauge galvanized steel and 20 gauge 316 L stainless steel. The galvanized steel conforms to ASTM A446/ A446M specifications.

3.3 Painted Coupons

Painted test coupons were prepared using the galvanized steel coupons and the following primer/paints.

- Rowe's Epoloid 7-W-20 Primer/Epoloid 5-G5 Finish.
- Wisconsin Protective Coating's Plasite No. 7100/ Anti-Corrosive Primer/Plasite No. 7122 Finish.

The thickness of the primer coat and the finish coat of each of the painted coupons was determined using a micrometer. For the Plasite coated coupons the mean primer thickness was 2.95 mils and the mean thickness of the finish coating was 4.80 mils. For the Epoloid coated coupons, the mean primer thickness was 2.46 mils and the mean thickness of the finish coating was 3.52 mils.

3.4 Decontaminants

3.4.1 Na_2CO_3

Reagent grade sodium carbonate (Mallinckrodt #7521) was dissolved in distilled water to form a 10 weight percent solution of Na_2CO_3.

3.4.2 NaOH

Reagent grade sodium hydroxide pellets (Baker #3722-5) was dissolved in distilled water to form a one weight percent solution of NaOH.

3.4.3 NaOCl

Household bleach (i.e., Clorox®), nominally 5% NaOCl, was used neat for the NaOCl solution. The solution was analyzed for available chlorine and weight percent NaOCl in accordance with ASTM D2022-64 (1980). The solution had 2.3 percent available chlorine (4.8 percent NaOCl).

4.0 TEST DESCRIPTION

4.1 Test Apparatus

The proposed decontaminant application system is described in Reference 3. A decontaminant solution, contained in a pressure vessel maintained at a pressure of 100 psig, was directed through three identical spray nozzles. The spray nozzles were oriented such that the spray from each nozzle completely covered one of the three test coupons (4-inch circle).

Each nozzle provided a spray of coarse water particles (150 to 750 microns in diameter) at a flow rate of about 0.24 gpm. This flow rate was maintained for a period of from one to two seconds for each spray application. As such, a coverage of about 0.05 gallons/ft^2/spray was achieved. The spray application was repeated 10 times at 5-minute intervals. Liquid from the spraying was drained into sump and then directed into a common collection vessel.

4.2 Analytical Baseline Determination

Prior to performance of the decontamination tests, analytical baseline tests were performed to 1) determine if interferences to agent analyses result when the coupons are extracted and 2) determine the recovery efficiency of the extraction procedure (i.e., the amount of spiked agent recoverable by the extraction procedure.

The absence of interferences to agent analyses was determined by extracting the painted coupons (no agent present). An aliquot of the extract was then analyzed using a gas chromatograph equipped with a flame photometric detector (GC/FPD) operating in either the sulfur mode (HD) or the phosphorus mode (GB and VX). The absence of peaks at the retention time of the agent would indicate that no interferences are present. The detection limit of the GC/FPD for each agent was 0.1 μg/ml.

Recovery efficiencies of the extraction procedure were determined as follows. A coupon was spiked with 10 mg munition grade HD, GB or VX using agent diluted with hexane. The concentrations of the dilute agent solutions were 1 mg VX/ml, 2 mg GB/ml or 10 mg HD/ml. Thus, in order to spike the coupon with 10 mg of agent, a total of 1 ml of dilute HD solution; 5 ml of dilute GB solution; or 10 ml or dilute VX solution was applied to each coupon. The solvent was allowed to evaporate and then the coupons were extracted. Each extract was analyzed for agent by GC/FPD. This analysis was compared with an analysis of a solution by GC/FPD containing a known concentration of agent which would be equivalent to that obtained if 100 percent of the agent spiked on the coupon could be recovered by extraction (i.e., 100 percent recovery). The recovery efficiency was then calculated as follows.

$$\text{Recovery efficiency} = \frac{\text{GC/FPD agent peak area from coupon extract}}{\text{GC/FPD agent peak area from 100 percent recovery}}$$

4.3 Decontamination Test Procedure

4.3.1 GB/10 Percent Na_2CO_3

For the first series of experiments three coupons clamped in coupon holders were each spiked with 10 mg of GB. The coupon holders were bolted into the test chamber and the chamber lid was secured. The coupons were then sprayed ten times at five minute intervals with ten percent Na_2CO_3 solution. The spray was maintained for one to two seconds during each interval. At completion of spraying about 20 ml of decontaminant solution/mg agent/coupon,

the spent solution in the sump was collected and the coupons were removed from the test chamber for analysis. The entire chamber was then rinsed with isopropyl alcohol and hexane. The rinses were collected for analysis. The rinses and the sump were analyzed to determine if undecomposed agent was physically removed from the coupons by the spray.

The decontaminated coupons were individually extracted by immersion in 50 mls of hexane for about five minutes. The hexane was collected and then concentrated to one ml using a Kuderna-Danish evaporative concentrator. The concentrate was analyzed using a GC/FPD operating in the phosphorus mode. Standard solutions containing known concentrations of GB (i.e., 0.1, 1 and 10 ppm) were analyzed before and after the coupon extracts. This was done to 1) prepare calibration curves, 2) determine that the instrument was functioning properly and that the sensitivity had not changed during the analyses and 3) identify the detection limit of the instrument. As such, the calibration curves provided assurances for quantitative analysis of agent in the sample.

The isopropyl alcohol/hexane rinses were concentrated and analyzed using the same method described for the coupon extracts.

Sumps samples were extracted with hexane in a two liter separatory funnel. The hexane was then concentrated and analyzed using the same method described for the coupon extracts.

4.3.2 GB/1 Percent NaOH

The test procedure, extraction and analysis methods for the experiments involving one percent NaOH as a decontaminant for GB were identical to the procedures described in Section 4.3.1.

4.3.3 HD/5 Percent NaOCl

The test procedure, extraction and analytical methods for the experiments involving five percent NaOCl solution as a decontaminant for HD were similar to the procedures described in Section 4.3.1. The one ml concentrate was analyzed using a gas chromatograph equipped with a flame photometric

detector (GC/FPD) operating in the sulfur mode. Standard solutions containing known concentrations of HD (i.e., 0.1, 1 and 10 ppm) were analyzed before and after the coupon extracts.

The isopropyl alcohol/hexane rinses were concentrated and analyzed using the same method described for the coupon extracts.

The sump samples were analyzed as follows. Prior to extraction, the residual NaOCl in the spent solution collected from the sump was neutralized using a 3 molar sodium arsenite solution. For each 50 ml of sump solution, 10.3 ml of 3 molar $NaAsO_2$ solution and 17 ml of 2.0 N NaOH solution were added. The neutralized solution was extracted with hexane in a two liter separatory funnel. The hexane was then concentrated and analyzed using the same method described for the coupon extracts.

4.3.4 VX/5 percent NaOCl

The test procedure, extraction and analytical methods for the experiments involving five percent NaOCl as a decontaminant for VX were similar to the procedures described in Section 4.3.3. The primary difference was that all glassware used for the VX analyses was pretreated with a silylating agent (REJUV-8®) prior to use.
Also, the GC/FPD was operated in the phosphorus mode for the VX analyses.

5.0 RESULTS/DISCUSSION OF RESULTS

5.1 Baseline Analytical Determination

Each of the four coupon types (i.e. UGS, USS, PES, PPS)* were extracted (no agent was spiked) using hexane. Analyses of the extracts by GC/FPD in the phosphorus and sulfur modes indicated no interferences are present for determination of HD, GB and VX.

* UGS = Unpainted Galvanized Steel, USS = Unpainted Stainless Steel, PES = Painted Epoloid Galvanized Steel, PPS = Painted Plastite Galvanized Steel.

Recovery efficiencies (i.e., the amount of spiked agent that can be recovered by extraction) for each of the four coupon types spiked with HD, GB or VX are given in Table 2. The results indicate that the agents can be efficiently extracted from each of the four types of test coupons. The recovery efficiencies were used to calculate residual agent on decontaminated coupons by the following expression:

$$\text{Residual Agent on Decontaminated Coupons (mg)} = \frac{\text{Result of GC Analysis(mg)}}{\text{Recovery Efficiency}}$$

5.2 GB/10% Na_2CO_3 Decontamination Test Results

Coupon decontamination results from the experiments in which ten percent Na_2CO_3 solution was sprayed on UGS, PES, USS and PPS coupons contaminated with GB are given in Table 3. The results suggest that 10 percent Na_2CO_3 solution is an effective decontaminant for GB on these materials. Effectiveness was demonstrated by the low or less than detectable levels of agent remaining on the coupons following the decontamination treatment.

Analyses of the sump liquid and rinses from the Na_2CO_3 decontamination experiments (See Table 4) suggest that if undecomposed GB was physically removed from the spiked coupons by the spray application of the Na_2CO_3 solution it was destroyed before analysis could be performed.

An important observation made during the GB decontamination tests which may impact on the selection of a decontaminant for GB was that a thick powdery film formed on all exposed internal surfaces of the test chamber (including the coupons) during experiments with Na_2CO_3 solution. Repeated attempts to remove the film by water wash were not successful. Complete removal was achieved only by washing with dilute sulfuric acid solution.

5.3 GB/1% NaOH Decontamination Test Results

Coupon decontamination results from the experiments in which one

TABLE 2. AGENT RECOVERY EFFICIENCIES FROM SPIKED COUPONS BY THE EXTRACTION METHOD

Agent	Coupon Type[a]	Experimental Recovery Efficiencies	Average Recovery Efficiency
HD	UGS	1.00	1.00
		1.00	
	USS	1.00	1.00
		1.00	
	PES	0.998	0.999
		1.00	
	PPS	0.98	0.98
		0.99	
GB	UGS	0.75	0.75
		0.76	
	USS	1.00	1.00
		1.00	
	PES	0.76	0.72
		0.68	
	PPS	0.84	0.87
		0.90	
VX	UGS	1.00	0.85
		0.71	
	USS	0.88	0.93
		0.99	
	PES	0.90	0.90
		0.90	
	PPS	0.94	0.93
		0.93	

(a) UGS = Unpainted Galvanized Steel
USS = Unpainted Stainless Steel
PES = Painted Epoloid Galvanized Steel
PPS = Painted Plasite Galvanized Steel

TABLE 3. COUPON DECONTAMINATION RESULTS (GB/NaOH, GB/Na_2CO_3)

Experiment Number	Agent	Decontaminant	Coupon Type[(a)]	Coupon Number[(b)]	Residual Agent on Decontaminated Coupon (mg)[(c)]	Decontamination Efficiency (%)[(d)]
1	GB	1% NaOH	UGS	-	0.0001	99.99
			PES	34	<0.0001[(e)]	>99.99
			USS	-	<0.0001	>99.99
2	GB	1% NaOH	PPS	13	<0.0001	>99.99
			UGS	-	0.0003	99.99
			PES	35	0.0015	99.98
3	GB	1% NaOH	PPS	12	<0.0001	>99.99
			USS	-	<0.0001	>99.99
			(f)	-	-	-
4	GB	10% Na_2CO_3	UGS	-	<0.0001	>99.99
			PES	37	<0.0001	>99.99
			USS	-	<0.0001	>99.99
5	GB	10% Na_2CO_3	PPS	12	<0.0001	>99.99
			UGS	-	0.0001	99.99
			PES	39	0.0003	99.99
6	GB	10% Na_2CO_3	PPS	15	<0.0001	>99.99
			USS	-	<0.0001	>99.99
			(f)	-	-	-

(a) UGS = Unpainted Galvanized Steel
PES = Painted Epoloid Galvanized Steel
USS = Unpainted Stainless Steel
PPS = Painted Plasite Galvanized Steel

(b) See Appendix C

(c) $\text{Residual Agent on Decontaminated Coupons (mg)} = \dfrac{\text{Result of GC Analysis (mg)}}{\text{Recovery Efficiency}}$

(d) The decontamination efficiency is the percent removal/destruction of agent from the coupon surface. Based on 10 mg of agent spiked on each coupon, the decontamination efficiency is given by:

$$\text{Decontamination Efficiency (\%)} = \left[\frac{10\text{ mg} - \text{Residual Agent on Decontaminated Coupon}}{10\text{ mg}}\right] \times 100$$

(e) The sign ">" implies less than the detection limit shown.

(f) A blank (not spiked) coupon was used as the third coupon in this test. The blank coupon was not analyzed.

TABLE 4. SUMP/RINSE ANALYSES FROM THE 12 JACADS EXPERIMENTS

Experiment Numbers	Agent	Decontaminant	Agent Found in Sump (mg)	Agent Found in Chamber Rinses (mg)
1	GB	1% NaOH	<0.0001[a]	<0.0001
2	GB	1% NaOH	<0.0001	<0.0001
3	GB	1% NaOH	<0.0001	<0.0001
4	GB	10% Na_2CO_3	<0.0001	<0.0001
5	GB	10% Na_2CO_3	<0.0001	<0.0001
6	GB	10% Na_2CO_3	<0.0001	<0.0001
7	HD	5% NaOCl	<0.0001	0.00072
8	HD	5% NaOCl	<0.0001	<0.0001
9	HD	5% NaOCl	(b)	0.00013
10	VX	5% NaOCl	<0.0001	0.002
11	VX	5% NaOCl	<0.0001	0.0005
12	VX	5% NaOCl	<0.0001	<0.0001

(a) The sign "<" implies less than the detection limit shown.

(b) Sample was discarded prior to analysis.

percent NaOH solution was sprayed on UGS, PES, USS and PPS coupons contaminated with GB are given in Table 3. The results suggest that 1 percent NaOH solution is an effective decontaminant for these materials. Effectiveness was demonstrated by the low or less than detectable levels of agent remaining on the coupons following the decontamination treatment.

Analyses of the sump liquid and rinses from the NaOH decontamination experiments (See Table 4) suggest that if undecomposed GB was physically removed from the spiked coupons by the spray application of the NaOH solution it was decomposed in the sump before analysis was performed.

In contrast to the Na_2CO_3 experiments, no film was formed on the exposed interval surfaces of the test chamber during the NaOH experiments.

5.4 HD/5% NaOCl Decontamination Test Results

Coupon decontamination results from the experiments in which five percent NaOCl solution was sprayed on UGS, PES, USS and PPS coupons contaminated with HD are given in Table 5. The results suggest that 5 percent NaOCl solution is an effective decontaminant for these materials. Effectiveness was demonstrated by the low or less than detectable levels of agent remaining on most of the coupons following the decontamination treatment. An exception is in Experiment Number 8 in which 0.1 mg of HD was found on the PES coupon following decontamination (as compared with 10 mg initially spiked).

Analyses of the sump liquids from the NaOCl/HD decontamination experiments (See Table 4) suggest that if undecomposed HD was washed from the coupons and collected in the sump it was decomposed before analyses was completed. However, undecomposed HD was found in the chamber rinses from Experiments 7 and 9. This suggests that a potential exists for contaminating previously clean surfaces with HD during decontamination by spraying NaOCl solution.

An important observation made during the NaOCl experiments which may impact on the selection of a decontaminant for HD and VX was that all

unpainted surfaces* exposed to NaOCl became slightly corroded. Corrosion was observed in each of the experiments which lasted approximately one hour. The supply vessel, test chamber and ancillary tubing were thoroughly cleaned following each NaOCl experiment by washing with dilute acid followed by several water rinses.

5.5 VX/5% NaOCl Decontamination Test Results

Coupon decontamination results from the experiments in which five percent NaOCl solution was sprayed on UGS, PES, USS and PPS coupons contaminated with VX are given in Table 5. The results suggest that 5 percent NaOCl solution is an effective decontaminant for these materials. Effectiveness was demonstrated in that all of the test coupons were decontaminated to below the detectable limit of the extraction method, equivalent to a 10^4 or greater reduction of the agent contamination.

Analyses of the sump liquids from the NaOCl/VX decontamination experiments (See Table 4) suggest that if undecomposed VX was washed from the coupons and collected in the sump it was decomposed before analysis was performed. However, undecomposed VX was found in the test chamber rinses from experiments 10 and 11. The data suggests that in this configuration contamination of previously clean surfaces with VX during spraying may occur.

6.0 CONCLUSIONS

Decontamination tests involving spray application of either 10 percent Na_2CO_3 solution or one percent NaOH solution on GB contaminated coupons and spray application of 5 percent NaOCl solution on either HD or VX contaminated coupons were performed. Results suggest that the decontaminants

* The NaOCl solution supply vessel was composed of 400 series stainless steel. The test chamber and ancillary tubing was composed of 304L stainless steel.

TABLE 5. COUPON DECONTAMINATION RESULTS (HD/NaOCl, VX/NaOCl)

Experiment Number	Agent	Decontaminant	Coupon Type[(a)]	Coupon Number[(b)]	Residual Agent on Decontaminated Coupon (mg)[(c)]	Decontamination Efficiency (%)[(d)]
7	HD	5% NaOCl	UGS	-	<0.0001	>99.99
			PES	33	<0.0001	>99.99
			USS	-	<0.0001	>99.99
8	HD	5% NaOCl	PPS	11	0.0006	99.99
			UGS	-	<0.0001	>99.99
			PES	22	0.1	99
9	HD	5% NaOCl	PPS	10	<0.0001	>99.99
			USS	-	<0.0001	>99.99
			(f)	-	-	-
10	VX	5% NaOCl	UGS	-	<0.0002	>99.99
			PES	31	<0.0002	>99.99
			USS	-	<0.0002	>99.99
11	VX	5% NaOCl	PPS	9	<0.0002	>99.99
			UGS	-	<0.0002	>99.99
			PES	32	<0.0002	>99.99
12	VX	5% NaOCl	PPS	8	<0.0002	>99.99
			USS	-	~0.0002	>99.99
			(f)	-	-	-

(a) UGS = Unpainted Galvanized Steel
PES = Painted Epoloid Galvanized Steel
USS = Unpainted Stainless Steel
PPS = Painted Plasite Galvanized Steel

(b) See Appendix C

(c) Residual Agent on Decontaminated Coupons (mg) $= \dfrac{\text{Result of GC Analysis (mg)}}{\text{Recovery Efficiency}}$

(d) The decontamination efficiency is the percent removal/destruction of agent from the coupon surface. Based on 10 mg of agent spiked on each coupon, the decontamination efficiency is given by:

$$\text{Decontamination Efficiency (\%)} = \left[\frac{10\text{ mg} - \text{Residual Agent on Decontaminated Coupon}}{10\text{ mg}}\right] \times 100$$

(e) The sign "<" implies less than the detection limit shown.

(f) A blank (not spiked) coupon was used as the third coupon in this test. The blank coupon was not analyzed.

effectively decontaminated unpainted 316L stainless steel, unpainted falvanized steel, Epoloid painted galvanized steel and Plasite painted galvanized steel contaminated with HD, GB or VX. Effectiveness was demonstrated by the low or less than detectable levels of agent remaining on the coupons following the decontamination treatment.

7.0 REFERENCES

(1) See Appendix A.

(2) CAMDS Test Report #46-12, December 20, 1983 and CAMDS Test Report #32-10, February 28, 1983.

(3) "Task 3, Subtask 5 Test Report on Stainless Steel Surface Decontamination Screening", See Appendix IV.

APPENDIX A

LITERATURE REVIEW

APPENDIX A

LITERATURE REVIEW

The literature searches which were performed to determine the existing data base included (1) a search of the abstracts and papers obtained from Phase I efforts under Contract No. DAAK11-81-C-0101*, and (2) a DTIC search focusing on hypochlorite and carbonate decontaminants. Abstracts and papers identified in these searches were then reviewed for pertinent papers or abstracts, i.e., those in which actual decontamination data for the decontaminants of interest were reported. In the case of decontamination with sodium hypochlorite, the search was expanded to include decontamination with solutions of either NaOCl, $Ca(OCl)_2$, or HTH (high test hypochlorite) since the reaction mechanism involving the OCl^- ion would likely be the same in each case. However, the search did not include either STB (supertropical bleach) or other hypochlorite-based slurries since the mechanism by which a slurry decontaminates is probably different from the mechanism by which an aqueous solution decontaminates.

Literature Review Results

Table A-1 summarizes the existing data base obtained from the literature review. A brief summary of the excerpts follows.

HD

Lewis (1981) showed that Clorox® resulted in 85 percent decomposition of mustard in 15 minutes. However, maintaining HD in contact with Clorox® for longer times (i.e., six hours) did not increase the percent decomposition of HD.

Anonymous (1971) demonstrated that a 10 percent HTH solution decomposed HD resulting in a decrease of HD concentration from an initial 20,000 ppm to a final concentration of 0.2 ppm.

* See "Development of Novel Decontamination Techniques for Chemical Agents (GB, VX, HD) Contaminated Facilities", by H. M. Grotta et al, Volume I, AD-B073 052L, February 1983, for a complete list of data bases searched in Phase I.

TABLE A-1. SUMMARY OF EXISTING DECONTAMINANT DATA BASE

Agent / Type of Spill	HD (5% Bleach)	GB (10% Carbonate)	VX (5% Bleach)
DPE Smear			
Wetted Steel Surface			(2)
Wetted Painted Concrete Surface			
Major Spill	X(1)	X(1)	X(1)

(1) Assumes data from experiments performed in mixed reactors (e.g., beakers) can be correlated to decontamination of major spills.

(2) Data on the decontamination of painted steel with an aqueous $Ca(OCl)_2$ solution has been reported [Miller (1964), Hott (1965)].

VX

Anonymous (1971) demonstrated that a 10 percent HTH solution decomposed VX resulting in a decrease of VX concentration from an initial 20,000 ppm to below the detectable limit.

Miller (1964) used a 5 percent $Ca(OCl)_2$ solution to decontaminate wetted painted steel contaminated with VX. Destruction efficiencies are given in the confidential report.

Hott (1965) reported that an aqueous $Ca(OCl)_2$ solution resulted in decontamination of wetted painted steel contaminated with VX to below the detectable limit.

Thomas (1977) indicated that a 10 percent aqueous solution of HTH achieved greater than 99 percent destruction efficiencies of VX when the molar ratio of $Ca(OCl)_2$ to VX was 7.3 to 1.

GB

Anonymous (1971) showed that a 10 percent solution of sodium carbonate resulted in the decomposition of GB to a final composition of about 0.004 μg/ml.

Torrisi (1977) indicated that the half life of GB in a 10 weight percent aqueous solution of Na_2CO_3 was about 15.6 seconds. The final GB concentration in solution was found to be less than 5 nanograms/ml.

Davis (1977) performed kinetic experiments on the destruction of GB by aqueous Na_2CO_3 solution. The half life of GB in Na_2CO_3 solution was determined to be 8.45 ± 0.51 seconds.

Discussion of Results

In general, little information was located on decontamination of the specific matrices of interest (e.g., painted concrete) with hypochlorite solutions (HD and VX) or sodium carbonate solutions (GB). However, if it is assumed that agent decomposition data obtained in well-mixed vessels simulates the condition encountered when decontaminating major spills, then the major spill category of Table 1 can be completely filled (i.e., sufficient data exists).

The potential problem in extrapolating vessel data to decontamination of spills is the mass transfer limitations which may occur as a result of incomplete mixing of the decontaminant with the agent spill. For example, since HD has a low solubility in water, the decomposition of HD by an aqueous hypochlorite solution is probably a heterogeneous (i.e., two-phase) reaction. As such, the reaction rate will be affected by mass transfer of the decontaminant (OCl^- ion) from the aqueous phase to the HD phase. A much lower reaction rate and, possibly, decontamination effectiveness, may result if the decontaminating solution is not sufficiently mixed with the agent spill. Mixing must be considered when the method by which the decontaminant is applied to the spill is specified. Another consideration is that the hypochlorite solution may cover the agent spill and give a false reading of complete decontamination if air sampling is the method used to determine decontamination effectivness. It is also important to note that the minimum amount of hypochlorite required for decontamination is dependent on the available chlorine content of the solution. A 10 weight percent HTH* solution used in several of the reported experiments contains about 7 percent available chlorine whereas a 5 weight percent NaOCl solution contains only about 2 percent available chlorine.

Other than for major spills, the only other category for which decontamination data is available is for decontamination of wetted steel contaminated with VX [Miller (1964), Hott (1965)]. Although the experiments were performed using wetted painted steel, it is anticipated that similar decontamination efficiencies would be obtained for wetted unpainted steel. The results, however, may not apply to decontamination of painted concrete because in the case of concrete, agent may permeate through the paint layer and into the porous concrete matrix.

Knowledge Gaps

Based on the literature review, the knowledge gaps that exist in the data base include the adequacy of:

* HTH typically contains 65 to 70 percent available chlorine.

- decontamination of wetted painted concrete and DPE smears contaminated with either HD or VX using NaOCl bleach,
- decontamination of DPE smears, wetted steel or wetted painted concrete contaminated with GB using 10 percent sodium carbonate,
- decontamination of wetted steel contaminated with HD using 5 percent NaOCl,
- correlating agent decomposition data obtained in vessel experiments with conditions encountered when decontaminating a major spill.

Other than determining the feasibility of correlating the vessel experiments with a major spill, experimentation is required to address the knowledge gaps. A review of the procedures by which the decontaminating solutions are applied to major spills may allow determination of the feasibility of correlating the vessel data with major spills.

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APPENDIX IX

ANALYTICAL METHODOLOGY
IN SUPPORT OF TASK 3

REPORT ON

SUMMARY OF ANALYTICAL METHODOLOGY
IN SUPPORT OF TASK 3,
LABORATORY EVALUATION OF NOVEL AGENT
DECONTAMINATION CONCEPTS
DAAK11-81-C-0101

to

UNITED STATES ARMY
TOXIC AND HAZARDOUS MATERIALS AGENCY

by

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Executive Summary

The utility of the extraction/gas chromatography method of analysis for determining residual HD, GB, or VX in or on matrices representative of those found in agent contaminated structures has been demonstrated during this research and development program. It has been used instead of the air sampling-impinger/colorimetric enzyme method of analysis currently accepted by the Army. The extraction procedure proved to be rapid and was reliable enough to demonstrate the effectiveness of various substrate decontamination concepts. This report summarizes the development of the analytical methodology used in support of Task 3.

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TEST REPORT

FOR

SUMMARY OF ANALYTICAL METHODOLOGY IN SUPPORT OF TASK 3, LABORATORY EVALUATION OF NOVEL AGENT DECONTAMINATION CONCEPTS

Contract No. DAAK11-81-C-0101

to

UNITED STATES ARMY
TOXIC AND HAZARDOUS MATERIALS AGENCY

1.0 INTRODUCTION

1.1 Goals of the Novel Processing Technology Program

The Novel Processing Technology Program was undertaken with the objective of demonstrating the effectiveness of various decontamination concepts for the destruction/removal of contamination found in Army structures and facilities. In Task 3 the contaminants of concern were the chemical agents GB, VX, and HD. The substrates to be decontaminated were stainless steel, mild steel (painted and unpainted), concrete (painted and unpainted), and unglazed porcelain. The decontamination concepts being evaluated are based on thermal and chemical reaction processes. The chemical decontamination methods were also screened for their reaction products.

The analytical methodology development work was performed in support of experimental activity. The decontamination concept development tasks were driven by the need to demonstrate at least 99.9 percent removal of agent from a substrate so that the concept decontamination effectiveness

could be assessed. Determination of the minimum amount of agent that had to be spiked onto the substrate in order to demonstrate at least 99.9 percent removal was dependent upon the detection limit of the analytical method and the demonstrated recovery of the agent by extraction from each substrate spiked at high and low levels. Because the recoveries from the various substrates were not the same for each agent, base line experiments had to be performed. The base line experimentation established average recoveries from each substrate and determined the presence of analytical interferences originating either from the substrate, the decomposition products or the painted surface. In addition to establishing recoveries from freshly spiked substrates, the analytical method development also had to concern itself with recoveries after prolonged period of contact with a potentially reactive substrate such as concrete. The fate of the chemical agents on concrete is the subject of Subtask 9 and is presented as part of this overall Task 3 report. Finally the analytical method used in the decontamination studies had to be reliable and rapid. Gas chromatography methods using either packed columns or capillary columns were only as reliable as the detection methods used to identify the chromatographed fractions. Early in this program flame ionization (FID) and later flame photometric (FPD) detection methods (sulfur or phosphorus mode) were used extensively. However, when there was some uncertainty in the analytical results based on retention time using FID or FPD, mass spectrometry was used to confirm the results.

1.2 Analytes and Matrices

The analytical method development for Task 3 addressed the determination of presence of small amounts the chemical agents HD, GB, and VX, in a number of matrices.

The matrices encountered in chemical decontamination screening tests (Subtask 3) consisted of water (condensed steam), monoethanolamine - water (50 percent), ammonia-water (ammonium hydroxide), anhydrous ammonia, and a 5 percent aqueous solution of 1-octylpyridinium 4-aldoxime bromide (OPAB). The procedures used to extract agent from these matrices and

the experimental equipment is summarized in Section 4, Subtask Methodologies.

The matrices used in substrate decontamination experiment in Subtasks 5 were stainless steel, and in Subtask 6, painted mild steel, unpainted mild steel, painted stainless steel, concrete, and unglazed porcelain tile. The surfaces were painted with a green primer (Krylon 1346) and forest green (Alkyd paint). In the Subtask 6 studies and especially those studies addressing the fate of agents on concrete, concrete coupons were used that were prepared under closely controlled proportions of sand, cement, and water and cured under controlled humidity. The 1/4-inch thick coupons, which contained no aggregate, were shown to be uniform in porosity and weight (e.g. average weight of 210 g with a relative standard deviation of 0.95 percent).

2.0 OBJECTIVES AND SCOPE OF THE ANALYTICAL METHOD DEVELOPMENT

The objective of the overall Novel Technology Program was to screen concepts for their decontamination effectiveness. It was a research and development program in which the performance of decontamination concepts were evaluated on a relative basis. The research and development nature of this work postponed any need for the USATHAMA Analytical Branch to certify the analytical methods employed throughout these evaluations. The Analytical Branch did, however, review the methods employed and approved their use in this research and development program.* A comparison of the analytical results from agent residues by the extraction method used in these studies with the results from a modified air-sampling method currently used by the Army was made at USATHAMA's request.

3.0 EXPERIMENTAL

3.1 Materials

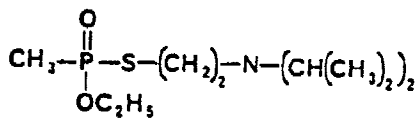
Two grades of chemical agent were used in these studies. Munition grade agent was used in all of the decontamination experiments and the

* Review presented to Ms. Robin L. Stein and Mr. Andrew P. Roach of USATHAMA at BCL on June 26, 1984.

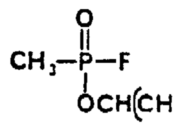
base line recovery experiments. The munition grade agents were compared with SARMS (PA 796, PA 1126, and PA 1128) by gas chromatography (GC) to determine their purity. Munition grade rather than high purity agent was selected for use in these studies because building contamination will most likely have originated from loading and handling of such materials. They were also considered to be the worst case situation since they contain stabilizers to inhibit degradation. The structures of the agents are as follows.

HD $Cl-(CH_2)_2-S-(CH_2)_2-Cl$

VX



GB



The matrices used in the decontamination experiments were 5-inch x 5-inch square coupons consisting of 14-guage mild steel, 14-guage 304 stainless steel, 1/4-inch thick concrete and unglazed porcelain. Steel coupons were painted with one coat of Krylon green primer No. 1346 (conforms to MIL-P-6585) and allowed to dry one to three hours before applying two coats of forest green alkyd paint NSN-8010-00-111-7937 (conforms to MIL-E--52798A) allowing 24 hours for each coat to dry. Painted coupons were cured for at least two weeks prior to use. Details for the preparation of concrete coupons are given in the Task 3 Subtask 4 test report. The unglazed porcelain coupons were cut from 6 x 6 x 1/4-inch tile using a tile cutter. The source was American-Olean Tile manufactured by the National Gypsum Company and purchased through Fisher Scientific. (Catalog No. 13-752)

3.2 Equipment

The determination of the amount of agent placed in/on or remaining in/on various matrices, required the use of gas chromatographs and the

Technicon Autoanalyzer. The following are the descriptions of the equipment used in this work and the rationale behind the changes in techniques to improve the detection limits.

3.2.1 Subtask 3: Chemical Concepts Preliminary Screening

(1) Varian Model 3700 GC was equipped with a packed column (using a 3 percent, SP 2100-DB on 100/120 Supelcoport) 6 feet long, 0.25 inches OD, 2mm ID. The detector was a Varian Flame Photometric Detector (FPD) that could be operated in the phosphorus (S) mode for determining GB and VX and the sulfur (S) mode for determining HD. Detection limit of this system is 5 microgram/ml for both GB and VX and 1 microgram/ml for HD.

(2) Finnagen Model A 1020 GC/MS used electron impact as the mode of ionization. The scan range and cycle time was 40-450 amu/second. A fused silica capillary column coated with DB-5 (30 meters x 0.025 mm) was used for GC separation and mass spectrometry (MS) was the detector used to identify the components in each fraction.

3.2.2 Subtask 5: Stainless Steel Surface Decontamination Screening

(1) Carlo Erba Gas Chromatograph equipped with a Flame Ionization Detection (FID) system (for HD).

(2) Hewlett Packard Gas Chromatograph equipped with a Flame Photometric Detection (FPD) system and Hewlett Packard Autosampler, used in phosphorus (P) mode (for GB and VX) and sulfur (S) mode (for HD). Both chromatographs were equipped with a 30 meter glass capillary column coated with SE-52 phase. The FPD system had a detection limit of 0.1 micrograms/ml for VX, and GB and 1.0 microgram/ml for HD.

(3) Impinger solutions used to collect HD were analyzed on a Varian 3700 GC equipped with a packed glass column (SP 1000 phase on Supelcoport) 6 feet long, 0.25 inch OD, 2mm ID, and utilizing a Hall Detector (electroconductivity detection) system.

(4) Impinger solutions used to collect VX or GB were analyzed using the Technicon Autoanalyzer II (enzymatic inhibition method using colorimetric detection). The detection limit for this system is .1 μg/ml VX and .2μg/ml GB but is sensitive to interferences.

3.2.3 Subtask 6: Steel/Concrete Decontamination Tests and Vapor Sampling Experiments

(1) Same as those listed in Subtask 5 above.

(2) In addition a Varian 3700 GC using a packed glass column (3 percent QF1 phase on Supelcoport) 6 ft long, 0.2500, 2mm ID and equipped with FPD system was used for GB and VX determination at Battelle's Hazardous Materials Laboratory (HML). The detection limit for this system is 5 microgram/ml.

(3) Another Varian 3700 GC using a packed glass column (SP 1000 phase) 6 ft long, 0.25 inch OD, 2 mm ID and equipped with a Hall Detector system was used for HD determination at the HML. The detection limit for this system is 0.05 microgram/ml.

The experiments in Subtask 3, the experiments late in Subtask 6, and the study on the fate of agent on concrete (Subtask 9) were performed in Battelle's Hazardous Materials Laboratory (HML) using neat agents. Therefore, spiking of matrices with agent could be done at levels so that a 99.99 percent destruction would still leave sufficient agent to be within the detection limit of the packed column GC/FPD systems.

When experiments were performed at Battelle's Toxic Substances Laboratory (TSL) early in the program (Subtask 5 and part of Subtask 6) surety restrictions kept the spiking levels to 0.0001 (or less) of those used at the HML. As such, significant improvements in the sensitivity of the gas chromatographic method were needed to demonstrate the desired 99.9 percent destruction at these much lower dose levels. This was accomplished as part of Subtask 5 where it was shown that the desired sensitivity was attainable for standardized dilutions of SARM HD, GB, and VX using a 30 meter glass capillary column coated with SE-52 phase (i.e., detection levels of 0.1 micrograms/ml for HD, GB, and VX).

3.3 Procedures

In both the base line experiments demonstrating recoveries by the extraction method and the subsequent analysis of the decontaminated matrices or substrates to demonstrate decontamination effectiveness, the following proceedures were used. Exceptions and special cases are outlined as part of the Subtask Methodologies (Section 4).

3.3.1 Spiking

Spiking of known amounts of agent on or in various matrices was performed using both nonsurety concentrations of agent in a solvent (hexane or methylene chloride) and neat agent. The procedures used to contaminate substrates of stainless steel, mild and painted steel surfaces were as follows.

Performance of experiments in the TSL required the use of dilute solutions of agent at the following maximum surety concentrations: VX = 1 mg/ml, GB = 2 mg/ml, and HD = 10 mg/ml.

The dilute agent solution was applied incrementally to the coupon and the solvent was allowed to evaporate after each increment in order to have a contaminated surface representative of field conditions (i.e., solvent not present).

The amount of solution required to spike the coupon was estimated as follows. Assuming that the solvent used to extract the coupon following the decontamination treatment is concentrated to a volume of 5 ml and a total of 10 microgram of agent is detectable by gas chromatography (GC).* Therefore, for determination of a destruction efficiency of about 99.9 percent, a total of 10 mg of agent must be initially applied to the coupon. A three order of magnitude difference between initial and anticipated final agent concentration is sufficient to allow determination of decontamination effectiveness. Higher destruction efficiencies may be extrapolated, if desired, either from the rate data obtained in the experiments or if the minimum detection level of the GC can be lowered to 0.1 ug/ml. Thus, in order to spike the coupon with 10 mg of agent, a total of 1 ml of dilute HD solution; 5 ml of dilute GB solution; or 10 ml of dilute VX solution must be applied to and the solvent evaporated from each coupon. Each incremental application was limited to just enough to cover the area to be spiked.

Neat agent, rather than solutions of agent in solvents, were used in chemical decontamination screening tests, and studies related to porous substrates such as the fate of agent on concrete and the decontamination of concrete and unglazed porcelain. Because these efforts were performed at the HML, larger amounts of agent could be spiked on or in to the matrices. This latitude provided the following benefits: (1) The less sensitive packed-column GC/FPD** could be used to demonstrate destruction efficiencies of 99.9 percent and (2) greater precision of the quanitity of agent dosed in to or on to the matrices is possible when larger volumes are measured and dispensed.

In the chemical concept prescreening study, neat agent was spiked directly into liquid decontamination solutions while stirring. The chemical decontamination prescreening experiments employing vapors of anyhdrous ammonia, ammonium hydroxide and water (i.e., gaseous reactants) required that a Teflon wool plug be spiked with 10 mg of the agent being studied.

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* Assuming that the minimum detection limit of GC for all agents is about 2 microgram/ml for a packed column GC.

** Minimum detection limit of 5 microgram/ml for GB and VX.

3.3.2 Agent Recovery by Extraction and Concentration

The analytical methodology required that the matrices be extracted with either methylene chloride or hexane. (The solvents were of spectroscopic purity purchased from Burdick and Jackson Laboratories, Inc. of Muskegon, Michigan.) Since agent may volatilize during spiking or adsorb on glass or metal surfaces, experiments had to be performed to determine the amount of applied agent that could be recovered by extraction after a spiking sequence. These base line experiments provided recovery efficiencies for each type of substrate used in the decontamination experiments. (Similar extractions of uncontaminated matrices provided samples for the identification of any interferences that could impair residual agent determination by this methodology.) Typically the 50 ml of solvent containing the extract is concentrated to 1 to 5 ml using a Kuderna-Danish evaporative concentrator prior to analysis by GC. Substrates spiked with neat agent were extracted with 150 ml of solvent and the extract usually analyzed without concentration.

3.3.2.1 Nonporous Coupons. In the base line experiments, various coupons were spiked with 10 mg of HD, GB, or VX using dilute solutions of the respective agent. After the solvent had evaporated, the coupons were extracted with 50 ml of either hexane or methylene chloride. The solvent was concentrated to a volume of one ml and the concentrate was analyzed for agent. Methylene chloride was not used to extract painted coupons because it softened the paint and also extracted components from the paint that proved to interfere with agent analysis by GC. For painted surfaces hexane was used. Results of the base line experiments, shown in Tables 1 and 2, are reported as recovery efficiencies. Recovery efficiency is the fraction of spiked agent recovered by extraction. The high recovery efficiencies shown in Tables 1 and 2 demonstrate that spiking coupons with dilute agent solutions was feasible. The average recovery

TABLE 1. AGENT RECOVERY EFFICIENCIES BY METHYLENE CHLORIDE EXTRACTION AFTER SPIKING STAINLESS STEEL COUPONS WITH DILUTE AGENT SOLUTIONS

Agent	Solution Spiked (ml)	Spiked Agent/ Coupon (mg)	Extracted Agent/ Coupon (mg)	Average Recovery Efficiency*
HD	1	10	10.4	0.85
			8.2	
			7.0	
GB	5	10	7.4	0.79
			8.8	
			7.5	
VX	10	10	5.4	0.58
			6.0	
			5.9	

$$* \text{ Average Recovery Efficiency} = \frac{\text{Average Agent recovered (mg)}}{10 \text{ mg}}$$

TABLE 2. AGENT RECOVERY EFFICIENCIES BY HEXANE EXTRACTION AFTER SPIKING ALKYD PAINTED STAINLESS STEEL AND UNPAINTED MILD STEEL WITH DILUTE AGENT SOLUTIONS

Agent	Material	Recovery Efficiency	Average Recovery Efficiency
HD	UMS[(a)]	0.94 0.95	0.94
HD	PSS[(b)]	0.92 0.89	0.90
GB	UMS	0.96 0.95	0.95
GB	PSS	0.83 0.85 0.85	0.84
VX	UMS	0.93 1.00	0.96
VX	PSS	0.50 0.57 0.60	0.56

(a) Unpainted mild steel
(b) Painted stainless steel (Note: This recovery efficiency was used for decontamination efficiency calculations on both painted stainless steel and painted mild steel coupons).

efficiencies, used in subsequent analyses to calculate the decontamination efficiency, were calculated as follows:

$$\text{Residual Agent on Decontaminated Coupon (mg)} = \frac{\text{Result of GC Analysis (mg)}}{\text{Recovery Efficiency}}$$

3.3.2.2 Liquid and Porous Substrates. These were the experiments involving neat agent in which liquid and gaseous chemical decontamination reactions were screened for effectiveness (Subtask 3) and in which porous substrates (i.e., concrete and unglazed porcelain) were contaminated/decontaminated (Subtask 6).

Liquid or Gaseous Reactant Substrates. Prior to beginning the experiments, several blanks and base line experiments were performed. A blank run with the gaseous-reactant application apparatus was done by refluxing hexane through the apparatus containing the Teflon wool plug. The extract was analyzed by GC for possible intereferences to agent determination.

Base line experiments with the gaseous-reactant application apparatus were done by placing 10 mg of VX on the Teflon wool plug and refluxing 30 ml of hexane through the apparatus for one hour. VX was chosen for this study because it was known to be the most tenacious (i.e., difficult to extract from glass) of the three agents. The 30 ml hexane extract was then analyzed for VX by GC and the recovery was found to be 108 percent. A second 30 ml of hexane was then refluxed through the apparatus and two aliquots were analyzed by GC and found to contain 0.42 percent of the original spike. The Teflon wool plug was then removed from the apparatus and extracted with methylene chloride. No agent was detectable in this extract.

Recovery efficiencies of agent from solutions of decontaminants using the procedures in Table 3 are given in Table 4. These recovery efficiencies represent the amount of agent that can be extracted from the decontaminant immediately following spiking of the solution with agent (i.e., time zero samples).

TABLE 3. SUMMARY OF EXPERIMENTAL PROCEDURES FOR EXTRACTION OF AGENT FROM LIQUID DECONTAMINANTS

Decontamination Concepts	GB	HD	VX
50% MEA	Acidify with acetic acid[e] Extract with CH_2Cl_2 Analyze by GC-MS[d]	Acidify with acetic acid[e] Extract with CH_2Cl_2 Analyze by GC-FPD[b]	Extract with CH_2CL_2 Analyze by GC-FPD[a]
100% MEA	Acidify with acetic acid[e] Extract with CH_2Cl_2 Analyze by GC-MS[d]	Acidify with acetic acid[e] Extract with CH_2Cl_2 Analyze by GC-FPD[b]	Extract with CH_2Cl_2 Analyze by GC-FPD[c]
Steam	Extract pot with CH_2Cl_2 Extract apparatus with hexane Extract wool with CH_2Cl_2 Analyze by GC-FPD[a]	Extract pot with CH_2Cl_2 Extract apparatus with hexane Extract wool with CH_2Cl_2 Analyze by GC-FPD[b]	Extract pot with CH_2Cl_2 Extract apparatus with hexane Extract wool with CH_2Cl_2 Analyze by GC-FPD[c]
Anhy. Ammonia	Same as steam	Same as steam	Same as steam
Ammonium Hydroxide	Same as steam[f]	Same as steam	Same as steam
OPAB	Extract with CH_2Cl_2 Analyze by GC-MS[d]	Extract with CH_2Cl_2 Analyze by GC-FPD[b]	Extract with CH_2Cl_2 Analyze by GC-FPD[c]

(a) Column: SP 2100; Program: 100 C (hold 1 minute) to 240 C at 90 C/minute; FPD detector; in P mode

(b) Column: SP 2100; Program: 135 C isothermal; FPD detector: in S mode

(c) Column: SP 2100; Program; 190 C (hold 4 minutes) to 240 C at 35 C/minute (hold 4 minutes); Detector in P mode

(d) Column: DB 5; Program: 35 C (1 minute hold) to 250 C at 12 C/minute (hold 2 minutes); Mass spectrometer: splitless, EI, range 40-450 amu/sec.

(e) To pH 3 using dilute acetic acid

(f) GC/MS analysis required because of analytical interferences with the GC-FPD approach

TABLE 4. RECOVERY EFFICIENCIES OF AGENT FROM DECONTAMINANTS

Agent	Decontaminant	Amount of Agent Spiked, mg	Amount of Agent Recovered,[a] mg	Recovery Efficiency,[b] %
HD	50% MEA	317	297.5	93.8
GB	50% MEA	287	39.9	13.9
VX	50% MEA	323	219.4[c]	68.5
VX	100% MEA	324	214.3[c]	66.1
HD	5% OPAB	279	371.3[c]	133.1
HD	5% OPAB	279	387.4[c]	138.9
GB	5% OPAB	283	(d)	(d)
VX	5% OPAB	282	88.3[c]	31.3
VX	5% OPAB	282	91.3[c]	32.4
GB	H_2O	10	5.24[c]	52.4
GB	NH_4OH	10	7.80[c]	78.0

a) The decontaminant solution was spiked with agent while stirring. A sample was immediately withdrawn and extracted with hexane or methylene chloride. The extract was then analyzed for agent using a gas chromatograph equipped with a flame photometric detector (GC/FPD).

b) Recovery efficiency (%) = 100 x (Agent recovered (mg) ÷ Agent spiked (mg))

c) Average of two analyses.

d) Interferences prevented the use of the GC/FPD. The samples were analyzed by a GC/mass spectrometer.

The base line experiments indicated that extraction of either HD or GB from MEA required acidiiication to pH 3 with acetic acid in order to achieve desirable recovery efficiencies. However, in the case of VX, extraction from MEA was performed without acidification. The recovery efficiency of VX from a 50 percent solution of MEA using methylene chloride was 109 percent without acidification while only 5.3 percent of the VX spiked was recovered upon acidification.

Porous Substrates. Early in Phase 1, an effort was made to demonstrate the utility of the extraction approach for the analysis of agent on concrete (i.e., a method development). GB and VX were found to be unrecoverable while HD showed some potential for recovery. A study to try to determine the fate of agents on concrete (Subtask 9) was undertaken as part of the Phase 2 effort. The results confirmed earlier findings that the GB and VX are not recoverable, while HD could be partially recovered. After a 24-hour (1440-minute) period in contact with concrete, recovery of HD spiked into concrete coupons at a loading of 1800 microgram/gram of concrete (average weight 10 coupons was 210 g, relative standard deviation = 0.95 percent) or 378 mg HD/coupon was determined using hexane or methylene chloride as extraction solvents. The coupons were crushed to pass through the neck of an Erlenmeyer flask equipped with a $ 24/40 ground glass joint (or 12 mm opening) prior to extraction. The results of the extraction of three coupons shortly after spiking and three coupons 24-hours after spiking are given in Table 5 for each solvent. It can be seen that methylene chloride is the better solvent of the two. Although the extraction after 24 hours is less than desirable, the recovery is still enough to demonstrate 99.9 percent decontamination because of the high spiking levels. As a worst case scenario, if only 1 percent of the 378 mg HD spiked is recovered by extraction using 150 ml methylene chloride, then a solution containing 25 micrograms/ml would be analyzed directly. Since the detection limit for HD is 0.05 microgram/ml by GC/Hall Detector,

TABLE 5. EXTRACTION RECOVERIES OF HD SPIKED ONTO CONCRETE FOR HEXANE AND METHYLENE CHLORIDE (Spiking Level 378 mg/210g coupon)

Coupon Number	Period after Spiking, min[a]	Recovered HD, percent
	Hexane, 150 ml	
1	0	30
2	0	22
3	0	33
4	1440	0.75
5	1440	0.10
6	1440	1.45
	Methylene Chloride, 150 ml	
7	0	57
8	0	59
9	0	60
10	1440	12.0
11	1440	2.0
12	1440	0.9

(a) Does not include the 30 minutes required to crush coupon for extraction.

98.7 percent destruction could be determined by analyzing the extract directly. Reduction of the 150 ml volume of extractant to 2 ml could have yielded a solution with a concentration of 1890 microgram/ml. Using the same detection level, determination of decontamination efficiencies of 99.99 percent are possible if the concentration step is incorporated into the procedure.

Because of the apparent reaction of GB and VX with concrete it was necessary to switch to a less reactive porous substrate in order to demonstrate a decontamination effectiveness by hot gases, steam, and OPAB solution. Unglazed porcelain tile which is <u>not</u> typical of any structural material found in any of Battelle's surveys of agent contaminated sites, was evaluated for reactivity toward GB and VX by the same procedure used to determine recoveries from concrete. The recoveries of agent spiked on the tile using hexane or methylene chloride as extraction solvents were determined shortly after spiking and after 24 hours. The spiking level again was 1800 microgram/gram of concrete. Since the average weight of 10 tiles was 216g, the amount of neat agent spiked onto each tile was 388 mg of GB or VX per tile. Initial attempts at recovering GB from intact tiles was unsuccessful (i.e., <1 percent recovery). When the tile was crushed and extracted with methylene chloride, two coupons immediately after spiking and the other two 24 hours later, the amount of agent recovered improved. The results are given in Table 6. The fact that recovery of GB is less than 1 percent after 1440 minutes suggests that decontamination efficiencies cannot be determined for GB in the experiments requiring a period of longer than 10 hours after spiking the coupon. However, other performance measures on the behavior of GB during early periods of the decontamination experiments by hot gases or steam can be made.

Results of the experiments to determine recoveries of VX spiked onto unglazed porcelain coupons using hexane and methylene chloride are given in Table 7. Methylene chloride is the better solvent yielding recoveries of VX of about 20 percent after 1440 hours. A 20 percent survival of

TABLE 6. EXTRACTION RECOVERIES OF GB FROM UNGLAZED PORCELAIN COUPONS

Expt	Solvent	Form	Time after Dosing, min	Recovery, percent
1	Hexane	Intact	0	<1
2	Hexane	Intact	0	<1
3	Methylene chloride	Crushed[a]	0[b]	21
4	Methylene chloride	Crushed	0	14
5	Methylene chloride	Crushed	1440	<1
6	Methylene chloride	Crushed	1440	<1

a) Crushed to pass through 12 mm opening in extraction flask

b) Includes 30 minutes needed to crush coupon

TABLE 7. EXTRACTION RECOVERIES OF VX FROM UNGLAZED PORCELAIN COUPONS USING HEXANE OR METHYLENE CHLORIDE (All Coupons Crushed to Less than 12mm)

Expt No.	Solvent	Time after Dosing, min.	Recovery Percent
1	Hexane	0[a]	60
2	Hexane	0	58
3	Hexane	0	46
4	Hexane	1440	3.7
5	Hexane	1440	<1
6	Hexane	1440	<1
8	Methylene Chloride	0[a]	78.1
9	Methylene Chloride	0	47.4
10	Methylene Chloride	1440	20
11	Methylene Chloride	1440	23.2

a) Includes 30 minutes needed to crush coupon

the VX spike after 24 hours would mean that 77.6 mg of the initial 388 mg of VX had survived. The coupon was extracted in 150 ml of methylene chloride to give a concentration of 517 microgram/ml. Since the detection limit of GC/FPD using a packed column (P mode) is 5 microgram/ml, decontamination efficiencies of >99.0 percent could be determined. Again, if the 150 ml volume of extract were reduced to 2 ml by concentration techniques, then the concentration of VX would be 38,775 micrograms/ml and a determination of 99.99 percent destruction efficiency is possible.

In several of the porous substrate experiments where no agent was detected, the extract was concentrated to either verify the absence or determine if a smaller amount were present but not detectable in the diluted extract solution.

3.4 Analytical Equipment

The analysis of the decontamination samples was performed as previously described for each concept. The equipment used for the sample analysis and the operating conditions at which the data was acquired are listed below:

- Instrument - Varian 3700 Gas Chromatograph
  - Detector - Varian Flame Photometric Detector
  - Gas Chromatography Column - 6 ft x 1/4 inch O.P. x 2 mm I.D. glass column
  - Column Packing - SP2100 3% on Supelcoport
  - Column Oven Conditions - 135 C isothermal for HD, 190 C (4 min/hold) program to 240 C at 35 C/minute for VX; 100 C (1 min/hold) program to 240 C at 90 C/minute for GB
  - Agents analyzed - HD, GB, VX
- Instrument - Varian 3700 Gas Chromatograph
  - Detector - Hall® 700A Electrolytic Conductivity Detector
  - Gas Chromatography Column - 6 ft x 1/4 1inch O.D. x 2 mm I.D. glass column

- Column Packing - SP1000 10% on Supelcoport
- Column Oven Conditions - 135 C isothermal
- Agents analyzed - HD

- Instrument - Carlo Erba 2100 Gas Chromatograph
  - Detector - Flame Ionization Detector
  - Gas Chromatography Column - 30 meter x .25 mm I.D. glass capillary column
  - Column Phase - SE-52 or equivalent phase 2-3 micron film thickness)
  - Column Oven Conditions 50 C (2 min/hold) program to 300 C at 10 C/min
  - Agents analyzed - HD, GB, VX
- Instrument - Hewlett Packard
  - Detector - Tracor Flame Photometric Detector
  - Gas Chromatography Column - 30 meter x .25 mm I.D. fused silica capillary column
  - Column Phase - SE-52 or equivalent phase 203 micron film thickness
  - Column Oven Conditions 50 C (2 min/hold) program to 300 C at 10 C/min
  - Agents analyzed - GB, VX, HD
- Instrument - Finnigan 1010 OWA
  - Detector - Mass Spectrometer

    Ionization mode - Electron impact

    Electron Voltage - 70 ev

    Scan Range - 40-450 amu

    Scan cycle time-1 sec
  - Gas Chromatography Column - 30 meter x .25 mm I.D. fused silica capillary column
  - Column Phase - DB-5 (J&W column

    2-3 micron film thickness)
  - Column Oven Conditions - 50 C (2 min/hold) program to 300 C

at 10 c/min
- Agents Analyzed - HD, GB, VX
- Instrument - Technicon® Autoanalyzer
  - Detector - Colorimeter
  - Detection System - enzyme inhibition of acetylthiocholinesterase, bovine erythrocyte (ACHE)
  - Agents analyzed - GB, VX

For all the gas chromatography techniques, a volume of 2 microliters of sample or standard was injected into the chromatography system. All instrumentation was calibrated daily using standard solutions prepared from working agent stocks. The detection limit of the detection system was determined as the low level calibration standard for eacn analytical system. The method detection limit was based upon the detection limit of the instrument and the calculated recovery of the sampling method.

4.0 SPECIFIC SUBTASK METHODOLOGIES

Each experiment within a subtask had its own specific analytical methodology. The methodology had to include: (1) methods used to quench chemical decontamination and recover unreacted agent; (2) methods used to determine at least qualitatively the path or fate of agents during chamber decontamination studies, i.e., tudies incorporating hot gas, steam, vapor circulation, flashblast, ventilation, and OPAB decontamination process; (3) determine interferences from decontaminants, their products, or the substrates under study; and (4)methods used perform decontamination validation experiments using Army protocols.

Methodology in this frame work encompasses selection and utilization of an appropriate number of impingers and selection of the proper solutions to be used in the impingers that are compatible with acceptable analytical methods. It encompasses the selection of the most reliable way to collect decontamination products, condensates, etc. and to wash down the walls

of the chamber and collect them in such a way that they can be analyzed. The following summaries from each subtask report in which a chamber was used identify specific operations that eventually lead to the analysis for agent on matrices not spiked directly.

4.1 Experiments with Gaseous, Aqueous Solution, Or Liquid Decontaminants (Subtask 3)

4.1.1 50 Percent MEA Water Solution

After adding the agent to a continuously stirred beaker containing 50 percent monoethanolamine and distilled water, 5-ml aliquots of the stirred mixture were removed at intervals of 10, 20, 40, 60, 120, 240, and 1440 minutes and extracted once with 5 ml of methylene chloride. As shown in Table 3, VX was the only agent that was extracted with methylene chloride without first treating the aliquot with 40 ml of 63 percent acetic acid to bring the solution to a pH 3. Both GB and HD aliquots required this treatment. The extracts of the aliquots were analyzed by GC-FPD using either the P mode or S mode. Because the apparent absence of GB destruction as measured by the retention time using GC-FPD, a GC-MS analysis of the extracts from a repeat experiment was done to determine if GB survived. The analysis showed that GB was destroyed and the decomposition product had a retention time identical to GB during gas chromatography.

4.1.2 100 Percent MEA

These experiments were performed similar to the 50 percent MEA experiments. The 5-ml aliquots were removed at predetermined intervals after addition of the agent. Those aliquots removed from experiments using GB and HD were acidified with 40 ml of acetic acid before a single extraction with 5 ml of methylene chloride. Aliquots removed from the VX experiments were extracted directly and analyzed using GC-FPD (as was

the extract from HD). GC-MS was used to analyze the extracts from the GB and the VX experiments for the reaction products.

4.1.3 OPAB Experiments

Two formulations of OPAB were used in these experiments. As the active components of the formulation, one contained a sodium salt of 1-octylpyridinium 4-aldoxime bromide, the other simply the OPAB compound dissolved in water. The agent was added to the stirred solution of OPAB and 10-ml aliquots were removed at intervals of 20, 40, 60, 180, 240, 360, and 1440 minutes. The aliquots were extracted once with 10 ml methylene chloride and the extract analyzed. For aliquots from the experiments involving HD and VX, the extracts were analyzed by GC-FPD. For the GB studies, GC-MS also had to be used in the analysis. Supplemental GC-MS spectra were obtained of the extracts from the OPAB/VX and OPAB/HD experiments to determine some of the reaction products.

4.1.4 Steam Experiments

In an apparatus designed for exposure of agent supported on a Teflon wool plug to gases or vapors, the agent was treated with steam generated in a flask. The condensate was returned to the flask without contacting the Teflon plug. After allowing the flask to cool, a 5-ml aliquot of the water collected in the flask after each refluxing period was taken at intervals of 5, 20, 60, and 120 minutes. The aliquots were extracted 5 ml of methylene chloride. After the reaction was completed, 30 ml of hexane contained in a fresh flask replaced the water flask and then refluxed for one hour and saved. The Teflon plug was then removed and extracted with 5 ml of methylene chloride. Decontamination effectiveness was determined by analyzing extracts of the condensates, the hexane rinse and the extract of the plug by GC-FPD for GB, VX, and HD. Major decontamination products contained in the extracts from the condensate were determined by GC-MS.

4.1.5 Anhydrous Ammonia

After contacting the agent loaded on the Teflon wool plug with ammonia vapor for periods of 20, 60, and 120 minutes, the ammonia was allowed to evaporate from the apparatus. After each such exposure the flask was extracted with 5 ml of methylene chloride. A hexane reflux of the equipment followed by a 5 ml methylene chloride extraction of the Teflon wool plug were also collected and analyzed. Destruction effectiveness was determined for GB, VX, or HD from analyses performed by GC-FPD in the three extracts. The reaction products from the VX/NH_3 decontamination reaction were extracted from the flask with 5 ml of methylene chloride and then analyzed by GC-MS.

4.1.6 Ammonium Hydroxide (NH_3/Steam)

These experiments were performed in the manner similar to the steam experiments. However, a reflux period of only 60 minutes was used. The condensate in the flask was extracted with 5 ml of methylene chloride. A hexane reflux rinse (30 ml) of the apparatus was collected and the Teflon wool plug was extracted with 5 ml of methylene chloride. The respective extracts were analyzed for GB, VX, and HD by GC-FPD to determine destruction efficiencies. The condensate extracts were used to determine the products of decontamination from the GB and VX experiments by GC-MS.

4.2 Chamber Decontamination Experiments (Subtasks 5 and 6)

The chamber used in evaluating decontamination concepts was designed to perform substrate decontamination in triplicate. The design permitted collection of volatilized agent, of condensate and spray solution, and of agent diffusing through porous substrates. It was designed to be easily

rinsed with solvent, and the solvent collected for analysis. The combination of isopropyl alcohol and/or hexane rinse also served to decontaminate the chamber between experiments. The experiments performed in the chamber were undertaken to demonstrate the decontamination effectiveness of concepts employing hot gases, steam, FREON 113® vapor circulation, flashblast and OPAB spray. Experiments were also performed to determine the amount of agent lost from nonporous surfaces during ambient air circulation. The following describe the procedures used to sample and analyze for residual agent or their reaction products collected in impinger solutions, condensates collected liquid decontaminant and chamber rinse solutions. Substrates investigated are those cited earlier, i.e., stainless steel, mild steel, painted steel, concrete, and unglazed porcelain.

4.2.1 Coupons

Coupons that had been originally spiked with agent were removed from the chamber after the completion of the decontamination experiments according to the respective test plan procedures. The coupons were individually extracted by immersion in 50 ml of hexane. Methylene chloride was not used for extraction because it also extracted paint components that interfered with agent analysis by GC-FPD. The coupons were allowed to soak in hexane for 5 minutes. This hexane extract was collected and concentrated to one ml using a Kuderna-Danish evaporative concentrator prior to analysis by GC-FPD or if necessary by GC-MS. The procedure used to extract concrete and unglazed porcelain coupons was described earlier (Section 3.2.2.2).

Standard solutions containing known concentration of agent (i.e., 10 ppm, 1 ppm, 0.1 ppm) were regularly used for preparation of calibration curves. The standard solutions were analyzed at the same conditions as the sample extracts and usually interspersed with them when an autosampler was employed. Such a procedure also provided for a continuous performance check of the GC-FPD equipment.

4.2.2 Impingers

Impingers were used either to collect vaporized agent contained in the chamber exhaust stream (hot gas and Flashblast decontamination experiments and the vapor sampling and ventilation experiments). For the hot gas and Flashblast experiments, ethylene glycol diacetate (EGDA) liquid was used in impingers for HD experiments, while pH 3.7 distilled water was used in the GB and VX experiments. The acidic water is prepared using sulfuric acid. Since January, 1985, pH 4.5 water has been used in impingers during the hot gas experiments. This change was recommended by USATHAMA's Analytical Branch through the Program Technical Representative (COTR) as a new standing operation procedure (SOP) for impinger studies. Exhaust gas was drawn through the impinger train at a rate of 46 to 58 liters/min.

In those experiments where nonporous substrates (steel) were being decontaminated, 2-500 ml Greenberg-Smith impingers were used in series to capture the agent vaporized into the main compartment of the chamber. The solutions were combined and the volume recorded. Aliquots were taken for analysis or stored at -5 C until analyses could be performed. In those experiments where porous substrates were used, a pair of 25 ml impingers in series were also used to capture any agent that vaporized through the substrates and swept/drawn from the back compartment of the chamber at flow of about 5 liters/min. About 100 ml of liquid was used in each 500-ml impinger (also about 100 ml of glass beads) and 10 ml in each 25 ml impinger.

Aliquots of the EGDA were analyzed for HD using GC/Hall Detector without prior concentration. This method gave a detection limit of 0.2 microgram/ml. The pH 3.7 (and later pH 4.5) water was analyzed directly without concentration for the presence of VX or GB using the Technicon Industrial System Autoanalyzer®. This enzyme inhibition method gave a detection limit of 0.2 microgram/ml for GB and 0.02 microgram/ml for VX.

A pair of 500 ml impingers were used in the ventilation experiments in which agent vapor in equilibrium with the agent spiked on steel or

painted steel coupons was drawn from the chamber to determine losses from simple transpiration during the heat-up periods of the hot gas experiments. The volume of the contents of the impingers was measured and aliquots were taken for analysis of GB, VX, or HD. The EDGA aliquot containing HD was analyzed by GC-Hall Dectector and the pH 3.7 water containing GB or VX was analyzed by the Technicon Autoanalyzer.

A pair of 25-ml impingers were used in series to capture any residual agent vaporized from decontaminated coupons from the hot gas, steam, and OPAB experiments. During the vapor sampling tests, contaminated coupons that had been decontaminated by one of the three methods, were heated up to 60 C and sufficient heated air (60 C) was drawn through a chamber containing the coupon to provide a measure of the minimum time-weighted-averages (TWA) for the agent concentration in the stream air. The impinger solutions were then analyzed HD, GB, or VX without further concentration by GC-Hall Detector or Technicon Autoanalyzer.

The condensate recovered in the sump and impingers from the experiments in which FREON 113® vapor was used was concentrated to approximately 5 ml using a rotary vacuum evaporator. The volume was further reduced to 1 ml using the Kuderna-Danish concentrator. The concentrated liquid was analyzed for the respective agent by GC-FPD.

4.2.3 Condensates

The water condensates collected during the steam decontamination experiments and the water recovered from the hot gas decontamination experiments were combined at the end of the experiment and extracted with 3-50 ml portions of methylene chloride. The extracts were combined and concentrated to one ml using the Kuderna-Danish concentrator technique. The concentrated extract was analyzed by GC-FPD operating in either the P or S mode.

4.2.4 Chamber Washdown

After the completion of each experiment in the chamber, the walls and other exposed surfaces (including the lid) were washed down with either

hexane, alone or isopropyl alcohol followed by hexane. k'en no water was present hexane was found to be effective. However, in those experiments where aqueous solutions were used or water condensation had occurred, hexane was unable to remove the water from the walls and metal parts of the chamber. It was necessary to use isopropyl alcohol first to dissolve the water droplets in the alcohol and then rinse with hexane. Either the hexane wash or the water-isopropyl alcohol-hexane wach mixture were collected through the sump of the chamber compartments. The volume of the collected samples were reduced first by rotary vacuum evaporation to about 5 ml and then by Kuderna-Danish concentrators to 1 ml. When the isopropyl alcohol (bp 82.3 C)/hexane (bp 69 C) mixture was evaporated, the isopropyl alchol remained behind as the solvent for the agent removed during the washdown. The hexane or isopropyl alcohol samples were analyzed by GC/FPD operating in the S mode for HD and in the P mode for GB and VX.

5.0 PROBLEM AREAS AND THEIR RESOLUTION

Early difficulties (low sensitivity and selectivity) encountered using GC-FID (flame ionization detector) to analyze for the agent residues remaining after decontamination of the low level spikes of stainless steel were overcome with the dedication of a GC-FPD instrument.

In order to overcome the lack of the sensitivity of the flame ionization detector for determining the small quantities of agent remaining after decontamination of the low-level-spiked coupons, a 30-meter glass capillary column was incorporated with a flame photometric detection system. Its improved sensitivity, shown dramatically by comparison of Figure 1 with Figure 2, gave a detection limit of 0.1 microgram/ml for each agent. Battelle has shown that the glass capillary column is reliable for the determination of VX despite the tendency of this compound to adhere to untreated glass surfaces. This method of VX analysis is currently being used by USATHAMA.

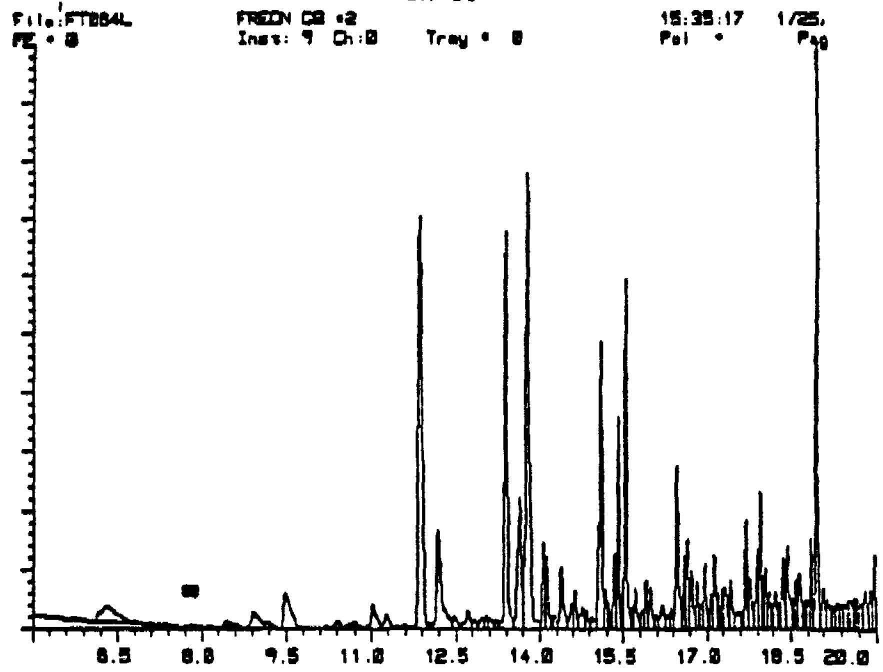

FIGURE 1. CAPILLARY COLUMN CHROMATOGRAPH OF GB IN FREON (FID)

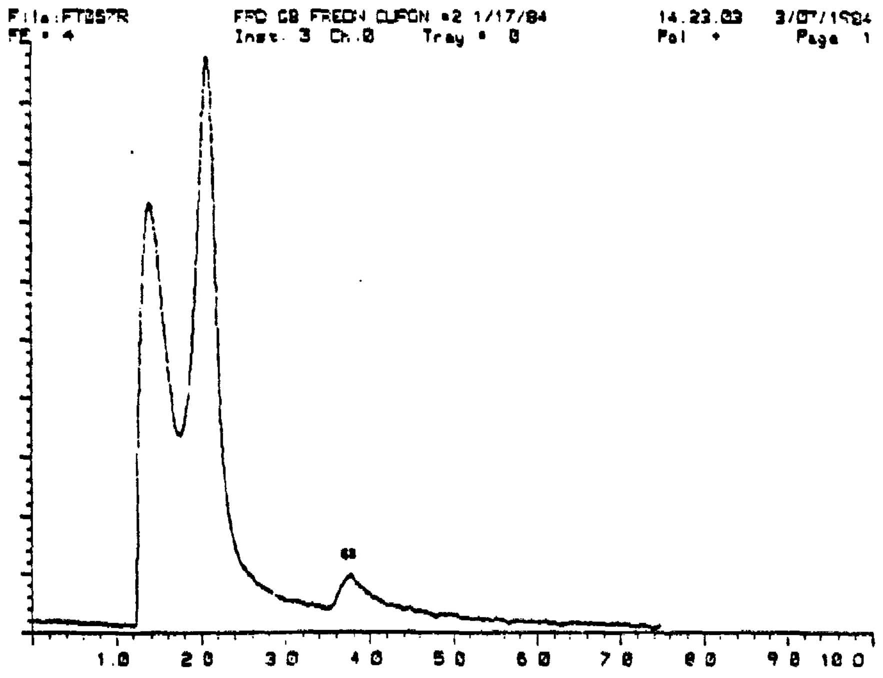

FIGURE 2. GLASS CAPILLARY COLUMN CHROMATOGRAPH OF THE SAME SAMPLE OF GB IN FREON (FPD)

6.0 CONCLUSIONS AND RECOMMENDATIONS

The analytical methodology based on the extraction of agent contaminated or treated substrates with hexane or methylene chloride is a viable alternative method to the vapor sampling method. It has been demonstrated to be reliable and reproducible when the samples are analyzed by GC-FPD for GB and VX and GC-Hall Detector for HD.

In any further demonstration of the effectiveness of structure decontamination processes in the field, and perhaps when it is necessary to demonstrate that residual agent has been removed from a structure. The Extraction/GC-FPD analytical method can prove to be a reliable alternative to the impinger-air sampling technique employing the less specific enzyme inhibition colorimetric method for analysis. For these reasons, Battelle recommends that the Extraction-GC method be considered for certification by USATHAMA as part of any future demonstration program.

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15 SEP 2006

MEMORANDUM TO Mr. Larry Downing, Defense Technical Information Center, 8725 John J. Kingman Road, Ft Belvoir, VA 22060-6218

SUBJECT: Downgrading from Limited Distribution to Unlimited Distribution

1. The following documents were reviewed, and it was determined by our Technical POC, Mr. Marty Stutz, that the distribution statement should be changed from limited to unlimited distribution.

a. AD Number: ADB073052: Development of Novel Decontamination Techniques for Chemical Agents (GB, VX, HD) Contaminated Facilities. Phase I. Identification and Evaluation of Novel Decontamination Concepts. Volume 1.
From Distribution Code 03 - US GOVERNMENT ONLY; DOD CONTROLLED to Distribution UNLIMITED, APPROVED FOR PUBLIC RELEASE.

b. AD Number: ADB073034: Development of Novel Decontamination Techniques for Chemical Agents (GB, VX, HD) Contaminated Facilities. Phase 1. Identification and Evaluation of Novel Decontamination Concepts. Volume 2.
From Distribution Code 02 - US GOVERNMENT AND THEIR CONTRACTORS to Distribution UNLIMITED, APPROVED FOR PUBLIC RELEASE.

c. AD Number: ADB093506: Development of Novel Decontamination Techniques for Chemical Agents (GB, VX, HD) Contaminated Facilities. Phase II. Laboratory Evaluation of Novel Agent Decontamination Concepts.
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d. AD Number: ADB087418: Development of Novel Decontamination and Inerting Techniques for Explosives Contaminated Facilities. Phase 1. Identification and Evaluation of Novel Decontamination Concepts. Volume 1.
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e. AD Number: ADB125304: Pilot Plant Testing of Hot Gas Building Decontamination Process.
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2. The POC is Ms. Janet Wallen, USAEC Records Manager, 410-436-6317.

FOR THE COMMANDER

SCOTT M. WINTER
MAJ, CM
Security Officer